Gregory Peck/DC/USEPA/US

01/01/2011 08:32 AM

To   Matthew Klasen

cc

bcc

Subject   Happy New Year!

OK - get out of the bed! Time to start 2011! Hope you had a good eve!

(b) (5)

Best,
Greg

ATTACHMENT REDACTED - DELIBERATIVE

2011-1-1 Mitigation Responses gep.docx

Christopher Hunter/DC/USEPA/US

01/01/2011 01:21 PM

To	"Tom Wall"
cc	
bcc	
Subject	Fw: Dec. 30 Working Draft of Spruce FD for Review/Comment

Hi Tom, here is the Spruce draft I circulated on Thursday afternoon.

Chris
Chris Hunter
US EPA, Wetlands Protection Division
(202) 566-1454 (t)
(202) 573-6478 (c)
   Christopher Hunter

----- Original Message -----
   From: Christopher Hunter
   Sent: 12/30/2010 05:10 PM EST
   To: Peter Silva; Nancy Stoner; Mike Shapiro
   Cc: Bob Sussman; Steven Neugeboren; Denise Keehner; Gregory Peck; Brian
Frazer; Avi Garbow; Arvin Ganesan; Christopher Hunter; Palmer Hough; Ross
Geredien; Julia McCarthy; Jordan Dorfman; Ann Campbell; Matthew Klasen; Shawn
Garvin; William Early; John Pomponio; Stefania Shamet; Kevin Minoli; Karyn
Wendelowski; David Evans; Jim Pendergast
   Subject: Dec. 30 Working Draft of Spruce FD for Review/Comment
Pete, Nancy, and Mike,

per Dave Evan's email last week, we are sending you the currently working draft of the Spruce No. 1 Mine
Final Determination for your review. It reflects all available comments received and is nearing final draft
status, with the exception of new material being generated in response to comments received on the
Region's Recommended Determination. If you have any comments before the briefing scheduled
Tuesday at 9:30am, please respond to me and I will incorporate them. Our current schedule is to accept
final comments no later than January 7, 2011 in order to prepare the final version by January 10.

ATTACHMENT REDACTED - DELIBERATIVE

Spruce FD 123010 clean draft.doc

Happy New Year and thanks again to everyone who has contributed to this effort.
Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Matthew Klasen/DC/USEPA/US

01/01/2011 06:23 PM

To Christopher Hunter

cc

bcc

Subject Fw: PD #78 fix

Hey Chris,

In the process of adding in edits from multiple folks on the RD comments, I noticed that Greg sent this to me as a PD fix. (If there were fewer comment-filled emails flying around, I'd have figured this out much more quickly!)

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

-----Forwarded by Matthew Klasen/DC/USEPA/US on 01/01/2011 06:21PM -----

To: Matthew Klasen/DC/USEPA/US@EPA
From: Greg Pond/R3/USEPA/US
Date: 12/31/2010 11:33AM
Cc: Stefania Shamet/R3/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA
Subject: PD #78 fix

Matt, (b) (5)

(See attached file: PD #78 makeover.doc)

Greg Pond
Office of Monitoring and Assessment
U.S. EPA Region 3
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
(p) 304-234-0243
(f) 304-234-0260
pond.greg@epa.gov

Website: http://epa.gov/reg3esd1/3ea50.htm   - PD #78 makeover.doc

ATTACHMENT REDACTED – DELIBERATIVE

Matthew Klasen/DC/USEPA/US
01/02/2011 12:17 PM

To Gregory Peck

cc

bcc

Subject Re: Can you send this note to Betsy & Joe (follow-up on Se)?

Yes, that looked good to me, and I agree that we'll have to address it. I've got this on my short list of things to talk about at 9:30 tomorrow morning

(b) (5)

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

-----Gregory Peck/DC/USEPA/US wrote: -----

To: Matthew Klasen/DC/USEPA/US@EPA
From: Gregory Peck/DC/USEPA/US
Date: 01/02/2011 12:14PM
Subject: Re: Can you send this note to Betsy & Joe (follow-up on Se)?

Sure.

(b) (5)

Thanks.

Gregory E. Peck
Chief of Staff
Office of Water
U.S. E.P.A.

From: Matthew Klasen
Sent: 01/02/2011 12:08 PM EST
To: Gregory Peck
Subject: Can you send this note to Betsy & Joe (follow-up on Se)?

Hey Greg,

Can you send the following note to Betsy and Joe, including the two attachments? We need them to weigh in on a selenium response. (b) (5)

██
████████████████████████████████████

Thanks,
Matt

TO: Betsy Behl/DC/USEPA/US, Joe Beaman/DC/USEPA/US,

CC: Charles Delos/DC/USEPA/US, Stefania Shamet/R3/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA, Frank Borsuk/R3/USEPA/US, Gregory Peck/DC/USEPA/US@EPA,

SUBJ: Fw: Spruce selenium response -- need your quick input on support for the 4 ppm whole body threshold

Betsy and Joe:

(b) (5)

To: Stefania Shamet/R3/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA, borsuk.frank@epa.gov
From: Frank Borsuk/R3/USEPA/US
Date: 12/29/2010 11:21AM
Cc: Matthew Klasen/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, David Rider/R3/USEPA/US@EPA, David Kargbo/R3/USEPA/US@EPA
Subject: Response Supplement #67 Selenium - Support for the 4 ppm whole body threshold

Stef:

Frank Borsuk, Ph.D.
Aquatic/Fisheries Biologist
Freshwater Biology Team
USEPA-Region 3 (Wheeling Office)
Office of Monitoring & Assessment (3EA50)
Environmental Assessment & Innovation Division
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
304-234-0241 Phone
304-234-0260 Fax
borsuk.frank@epa.gov

Please visit our website at http://epa.gov/reg3esd1/3ea50.htm

Matthew Klasen/DC/USEPA/US
01/02/2011 12:35 PM

To Matthew Klasen

cc

bcc

Subject

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780

cell (202) 380-7229 ⬜ - 2011-01-02 Compiled H&W RD Comment Responses.docx

ATTACHMENT REDACTED – DELIBERATIVE

To "Stefania Shamet"

cc

bcc

Subject Fw:

1 attachment

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responses.docx

Here's the most recent draft, for plugging in Se edits (or the Greg-Maggie edits edits, as appropriate).

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water
(202) 566-0780
Cell (202) 380-7229

From: Matthew Klasen
Sent: 01/02/2011 12:35 PM EST
To: Matthew Klasen

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Christopher
Hunter/DC/USEPA/US

01/02/2011 02:56 PM

To Palmer Hough

cc

bcc

Subject Re: Fw: Revised Spruce FD

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

-----Palmer Hough/DC/USEPA/US wrote: -----

To: "Chris Hunter" <hunter.christopher@epa.gov>
From: Palmer Hough/DC/USEPA/US
Date: 12/30/2010 08:09PM
Subject: Fw: Revised Spruce FD

Chris

Ann has made some excellant points here. Perhaps we can share these with Kevin and others. I think its important to think about this and discuss every issue in depth. Maybe Ann could join a call on the issue on monday?

Palmer

Sent from my BlackBerry Wireless Device

Palmer Hough, Environmental Scientist
Wetlands Division
U.S. EPA, Headquarters
tel: 202.566.1374

_____

From: Ann Williams (b) (6)
Sent: 12/30/2010 06:04 PM EST
To: Christopher Hunter
Cc: Ann Williams; Palmer Hough
Subject: Re: Revised Spruce FD

Ann

On Thu, Dec 30, 2010 at 5:15 PM, <Hunter.Christopher@epamail.epa.gov> wrote:
Happy New Year, Ann.

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| From:     |
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|Ann Williams <(b) (6)            >
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| To:       |
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 |Christopher Hunter/DC/USEPA/US@EPA
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 |Ann Williams/R1/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA
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 |12/29/2010 09:01 PM
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| Subject:   |
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 |Re: Revised Spruce FD
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Hi Chris and Palmer,

(b) (5)

Ann

On Wed, Dec 29, 2010 at 11:15 AM, <Hunter.Christopher@epamail.epa.gov>
wrote:

(b) (5)

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov


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| From:      |
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 |Ann Williams (b) (6)
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| To:        |
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 |Christopher Hunter/DC/USEPA/US@EPA
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 |Ann Williams/R1/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA
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  | Date:     |
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  |12/28/2010 09:57 PM
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  | Subject:   |
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  |Re: Revised Spruce FD
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Dear Chris and Palmer,

(b) (5)

(b) (5)

Ann

On Thu, Dec 23, 2010 at 12:34 PM, <Hunter.Christopher@epamail.epa.gov>
wrote:

 Hi Ann,

(b) (5)

Chris
(See attached file: Spruce FD 122210 draft.doc)

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed

(202) 566-1454
hunter.christopher@epa.gov
[attachment "Spruce FD 122210 draft(2)(AW edits).doc" deleted by
Christopher Hunter/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780

cell (202) 380-7229   - 2011-01-02 Compiled H&W RD Comment Responses.docx

ATTACHMENT REDACTED – DELIBERATIVE

Christopher Hunter/DC/USEPA/US

01/03/2011 07:45 AM

To Brian Topping, Palmer Hough

cc

bcc

Subject Fw: Mitigation section

Happy New Year, welcome back, and good morning,

(b) (5)

███
███████████████████████████████████
███████████████████████████

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

----- Forwarded by Christopher Hunter/DC/USEPA/US on 01/03/2011 07:40 AM -----

From:	Matthew Klasen/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Cc:	Stefania Shamet/R3/USEPA/US@EPA
Date:	01/02/2011 10:38 PM
Subject:	Re: Mitigation section

(b) (5) ██████████

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Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

To: Christopher Hunter/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA
From: Stefania Shamet/R3/USEPA/US
Date: 01/02/2011 08:44PM
Subject: Mitigation section

Matt, Chris -- Turns out the person John F. had in mind is unavailable. I know we're all swamped, but...

Can Brian and Palmer take a first cut and then Greg Pond or somebody in R3 could review? I'm not sure of Greg's availability tomorrow, so this may have to spill past Monday. It would help if we knew what the specific issues are. Thanks!

2010-01-02 Mitigation Comments-Responses of Potential Concern.docx 2011-01-02 Compiled H&W RD Comment Responses.docx

ATTACHMENTS REDACTED - DELIBERATIVE

Christopher Hunter/DC/USEPA/US

01/03/2011 07:47 AM

To   Julia McCarthy

cc

bcc

Subject   Fw: Final edits to FD Appendix 2 Macroinvertebrates

Can you take Greg's latest comments and incorporate them into the Appendix on the G drive? Also, see if anything needs to be corrected in the main body to match.

Thanks

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov
----- Forwarded by Christopher Hunter/DC/USEPA/US on 01/03/2011 07:47 AM -----

From:	Greg Pond/R3/USEPA/US
To:	Margaret Passmore/R3/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	12/31/2010 10:34 AM
Subject:	Final edits to FD Appendix 2 Macroinvertebrates

For Appendix 2, this final draft incorporates updated functional feeding group calculations and additionally, I inserted a few edits throughout the whole document. I used track changes.

ATTACHMENT REDACTED - DELIBERATIVE

Appendix_2_macroinvertebrates_123110_GP Final Edits.doc

These FFG changes were sent to Matt for RD response document yesterday, as #146A (even though I inadvertantly named it 149A re-do.doc--hopefully Matt caught that!). An update will be needed on PD FFG responses too. I am doing that now.

Greg

Greg Pond
Office of Monitoring and Assessment
U.S. EPA Region 3
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
(p) 304-234-0243
(f) 304-234-0260
pond.greg@epa.gov
Website: http://epa.gov/reg3esd1/3ea50.htm

Gregory Peck/DC/USEPA/US
01/03/2011 08:41 PM

To Matthew Klasen

cc

bcc

Subject Re: Re: Fw: 1/4/11Mining call agenda-call is MOVED to 10:30 to 11:30

Let's talk about this tomorrow.

Gregory E. Peck
Chief of Staff
Office of Water
U.S. E.P.A.

From: Matthew Klasen
Sent: 01/03/2011 08:36 PM EST
To: Gregory Peck
Subject: Fw: Re: Fw: 1/4/11Mining call agenda-call is MOVED to 10:30 to 11:30

FYI from Mike Slimak. (b) (5)

[redacted]

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229
-----Forwarded by Matthew Klasen/DC/USEPA/US on 01/03/2011 08:34PM -----

To: Michael Slimak/DC/USEPA/US@EPA
From: Matthew Klasen/DC/USEPA/US
Date: 01/03/2011 08:34PM
Cc: Susan Norton/DC/USEPA/US@EPA, Susan Cormier/CI/USEPA/US@EPA
Subject: Re: Fw: 1/4/11Mining call agenda-call is MOVED to 10:30 to 11:30

OK, that works - (b) (5)

[redacted]

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229
-----Michael Slimak/DC/USEPA/US wrote: -----

To: Matthew Klasen/DC/USEPA/US@EPA
From: Michael Slimak/DC/USEPA/US
Date: 01/03/2011 02:35PM
Cc: Susan Norton/DC/USEPA/US@EPA, Susan Cormier/CI/USEPA/US@EPA
Subject: Re: Fw: 1/4/11Mining call agenda-call is MOVED to 10:30 to 11:30

Yes, I can provide a brief summary of next steps. I don't plan to summarize the SAB reports.

Matthew Klasen---01/03/2011 02:24:58 PM---Hi Mike, I'd suggested to OWOW this morning that ORD could give a quick summary tomorrow morning of

From: Matthew Klasen/DC/USEPA/US
To: Michael Slimak/DC/USEPA/US@EPA
Cc: Susan Cormier/CI/USEPA/US@EPA, Glenn Suter/CI/USEPA/US@EPA, Jeff
Frithsen/DC/USEPA/US@EPA, Susan Norton/DC/USEPA/US@EPA
Date: 01/03/2011 02:24 PM
Subject: Fw: 1/4/11Mining call agenda-call is MOVED to 10:30 to 11:30

Hi Mike,

I'd suggested to OWOW this morning that ORD could give a quick summary tomorrow morning of the
updated SAB reports and next steps, and it's on the draft agenda for tomorrow morning (10:30-11:30.
Does that work for you?

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229
----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/03/2011 02:24 PM -----

Fro CynthiaN Johnson/DC/USEPA/US
m:
To: Ann Campbell/DC/USEPA/US@EPA, Ben Ghosh/R4/USEPA/US@EPA, Beth Walls/R4/USEPA/US@EPA,
    Bharat Mathur/R5/USEPA/US@EPA, Bob Sussman/DC/USEPA/US@EPA, Brian Frazer/DC/USEPA/US@EPA,
    Chris Thomas/R4/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Cliff
    Rader/DC/USEPA/US@EPA, Daniel Holliman/R4/USEPA/US@EPA, Darren Reid/DC/USEPA/US@EPA, David
    Evans/DC/USEPA/US@EPA, Denis Borum/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA,

Duncan Powell/R4/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA, Georgia
Bednar/DC/USEPA/US@EPA, Grace Robiou/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Janice
Donlon/R3/USEPA/US@EPA, Jeffrey Lapp/R3/USEPA/US@EPA, Jim Giattina/R4/USEPA/US@EPA, John
Forren/R3/USEPA/US@EPA, John Pomponio/R3/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Jordan
Dorfman/DC/USEPA/US@EPA, Justin Wright/DC/USEPA/US@EPA, Karyn
Wendelowski/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Kevin Pierard/R5/USEPA/US@EPA,
Larinda Tervelt/R4/USEPA/US@EPA, Mahri Monson/DC/USEPA/US@EPA, Marcus
Zobrist/DC/USEPA/US@EPA, Mark Nuhfer/R4/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA,
Melissa Raack/DC/USEPA/US@EPA, Michael Dunn/R3/USEPA/US@EPA, Michael
Slimak/DC/USEPA/US@EPA, MichaelG Lee/DC/USEPA/US@EPA, Naimah Karim/R5/USEPA/US@EPA, Nanci
Gelb/DC/USEPA/US@EPA, Nancy Stoner/DC/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA, Peter
Silva/DC/USEPA/US@EPA, Peter Swenson/R5/USEPA/US@EPA, Philip Mancusi-Ungaro/R4/USEPA/US@EPA,
Rebecca Cover/R4/USEPA/US@EPA, Robert Klepp/DC/USEPA/US@EPA, Rosemary
Hall/DC/USEPA/US@EPA, Ross Geredien/DC/USEPA/US@EPA, Sharmin Syed/DC/USEPA/US@EPA, Shawn
Garvin/R3/USEPA/US@EPA, Stan Meiburg/R4/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA,
Stephanie Fulton/R4/USEPA/US@EPA, Susan Cormier/CI/USEPA/US@EPA, Susan
Norton/DC/USEPA/US@EPA, Tanya Code/DC/USEPA/US@EPA, Timothy Landers/R6/USEPA/US@EPA, Tinka
Hyde/R5/USEPA/US@EPA, Todd Bowers/R4/USEPA/US@EPA, Tom Laverty/DC/USEPA/US@EPA, Tom
Welborn/R4/USEPA/US@EPA, Wendy Melgin/R5/USEPA/US@EPA, William Early/R3/USEPA/US, Elaine
Suriano/DC/USEPA/US@EPA, Caroline Whitehead/DC/USEPA/US@EPA, Amy Newbold/R4/USEPA/US@EPA,
Brian Topping/DC/USEPA/US@EPA, Bridget Staples/R4/USEPA/US@EPA, Eric
Somerville/R4/USEPA/US@EPA, Chad Harsh/R3/USEPA/US@EPA, Jessica Martinsen/R3/USEPA/US@EPA,
Susan Hansen/R4/USEPA/US@EPA, Tom Marshall/DC/USEPA/US@EPA, Larry Long/R4/USEPA/US@EPA,
Kip Tyler/R4/USEPA/US@EPA, Sonia Alteri/DC/USEPA/US@EPA, Glenn Suter/CI/USEPA/US@EPA

Date: 01/03/2011 11:06 AM

Subject: 1/4/11Mining call agenda-call is MOVED to 10:30 to 11:30

All,

I have attached the agenda for tomorrow's mining call. Please note that the call starts at 10:30 instead
of 10 tomorrow morning.

[attachment "Mining Call Agenda 1-4-11.doc" deleted by Michael Slimak/DC/USEPA/US]
--
Cynthia N. Johnson
Program Analyst
U.S. Environmental Protection Agency
Office of Wetlands, Oceans and Watersheds
Wetlands Division
Johnson.CynthiaN@EPA.gov
Phone: (202) 566-1679
Fax: (202) 566-1349

Mailing Address:
1200 Penn. Ave, NW MC: 4502T
Washington, DC 20460

Peter Silva/DC/USEPA/US 01/03/2011 10:46 AM	To	Gregory Peck
	cc	Mike Shapiro, Nancy Stoner
	bcc	
	Subject	Re: Key Spruce Policy Issues

thanks for the summary.

Peter S. Silva
Assistant Administrator
Environmental Protection Agency
Office of Water
Telephone: (202) 564-5700
FAX: (202) 564-0488

Mailing Address: 1200 Pennsylvania Ave., NW, Mail Code 4101M, Washington, DC 20460-0001

Physical/FedEx/Courier Address: 1201 Constitution Ave., NW, Rm. 3219 EPA East Building, Washington, DC 20004-3302

Gregory Peck	Pete: As we discussed this morning - here's a lis...	01/03/2011 10:42:03 AM

From:	Gregory Peck/DC/USEPA/US
To:	Peter Silva/DC/USEPA/US@EPA
Cc:	Nancy Stoner/DC/USEPA/US@EPA, Mike Shapiro/DC/USEPA/US@EPA
Date:	01/03/2011 10:42 AM
Subject:	Key Spruce Policy Issues

Pete:

As we discussed this morning - here's a list of key policy issues raised by the Spruce Mine Final Determination. With considerable help from OGC, I think we are reasonably good shape in anticipating and responding to key legal issues. Its some of the policy questions that will make communication of the Final Determination a challenge and about which we'll want to talk with you during our briefing tomorrow morning..We'll coordinate with Denise and OWOW and OGC to ensure this is the correct set of issues.

Best,
Greg

(b) (5)

Christopher Hunter/DC/USEPA/US

01/03/2011 11:01 AM

To Julia McCarthy

cc

bcc

Subject Last draft of macro appendix

ATTACHMENT REDACTED - DELIBERATIVE

Appendix 2 macroinvertebrates 122910.doc

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Matthew Klasen/DC/USEPA/US

01/03/2011 11:03 AM

To Christopher Hunter

cc

bcc

Subject RD comments 1-67 for cross-refs

Hey Chris,

So attached are 1) a PDF version of the current status spreadsheet, and 2) current draft responses to 1-67.

You'll see on the spreadsheet that I've marked each relevant comment "Needs cross-ref" or something similar ("Needs more cross-refs" or "Needs cross-ref review"). Ignore all the comments that say something else (e.g., "needs review").

I've also included a comment box in the actual draft that says "needs cross-ref" or the like.

Based on a quick count, comments needing references are **2, 3, 5, 7, 8, 10, 15, 16, 17, 24, 28, 37, 38, 40, 45, 51, 52, 57, and 66.**

I know there are a lot here, but let me know when you get a sense of how long this will take. Stef is planning on getting Se comments to me by 2 pm, which would mean I'd like to shoot for 3 pm if we can to get this packaged up and off to Kevin.

Thanks,
Matt

ATTACHMENT REDACTED – DELIBERATIVE

Spruce 1-67 for cross-refs.pdf   2011-01-03 RD Comments 1-67 for Cross-Refs.docx

----
Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Christopher Hunter/DC/USEPA/US

01/03/2011 11:42 AM

To Tanya Code

cc Brian Frazer, David Evans

bcc

Subject Materials for 1-4-11 Briefing

Hi Tanya,
here are the materials for tomorrow.

Thanks   Document Withheld-FOIA(b)(5)

Spruce 404(c) Executive Summary - 010311.docx 1-04-11 Briefing Agenda.docx Spruce Site Map.docx

Document Withheld-FOIA (b)(5)

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Left Fork Beech Creek

Dal-Tex Mine Complex

Spruce Fork

Seng Camp Creek

1A

1B

Spruce No. 1 Mine

Pigeonroost Branch

2A

3

2B

Trace Branch

4

Oldhouse Branch

White Oak Branch

Boone

Logan

0 0.25 0.5 1 Kilometers

0 0.25 0.5 1 Miles

Dal-Tex Mine Complex

WV Counties

Spruce No. 1 Mine

NHD24k Hydro

Valley Fill

N

Denise Keehner/DC/USEPA/US
Sent by: Tanya Code

01/03/2011 12:12 PM

To   Tanya Code

cc

bcc

Subject   Fw: Spruce Mine Key Policy Issues

Denise Keehner
Director
Office of Wetlands, Oceans, and Watersheds
Phone: 202-566-1146; Fax: 202-566-1147
Street address: 1301 Constitution Ave., N.W.
Room 7130E

----- Forwarded by Tanya Code/DC/USEPA/US on 01/03/2011 12:12 PM -----

From:	Gregory Peck/DC/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA, Brian Frazer/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Kevin Minoli
Cc:	Denise Keehner/DC/USEPA/US@EPA
Date:	01/03/2011 10:46 AM
Subject:	Spruce Mine Key Policy Issues

As we discussed this morning - here are a set of key policy/communications issues raised by the Spruce Mine 404(c). I think we'll want to include at least some discussion of these during the briefing for Pete tomorrow - and perhaps also with Bob. Please let me know if you have any suggested revisions to this list?

Thanks,
Greg

(b) (5)

Denise Keehner/DC/USEPA/US
Sent by: Tanya Code

01/03/2011 12:12 PM

To   Tanya Code

cc

bcc

Subject   Fw: Spruce Mine Key Policy Issues

Denise Keehner
Director
Office of Wetlands, Oceans, and Watersheds
Phone: 202-566-1146; Fax: 202-566-1147
Street address: 1301 Constitution Ave., N.W.
Room 7130E
----- Forwarded by Tanya Code/DC/USEPA/US on 01/03/2011 12:12 PM -----

From:	Gregory Peck/DC/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA, Brian Frazer/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Kevin Minoli
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Subject:	Spruce Mine Key Policy Issues

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Thanks,
Greg

(b) (5)

Christopher Hunter/DC/USEPA/US

01/03/2011 01:48 PM

To   Stefania Shamet

cc

bcc

Subject   Re: JUST WHEN YOU THINK YOU'RE DONE WITH THE PD COMMENTS ...Fw: Addition to the PD #13 concerning No Effect on Birds Comment (by EPA-Frank Borsuk)

(b) (5)

███

| Stefania Shamet | I just pointed out to somebody that the good new... | 01/03/2011 01:45:54 PM |

From: Stefania Shamet/R3/USEPA/US
To: Christopher Hunter/DC/USEPA/US@EPA
Date: 01/03/2011 01:45 PM
Subject: Re: JUST WHEN YOU THINK YOU'RE DONE WITH THE PD COMMENTS ...Fw: Addition to the PD #13 concerning No Effect on Birds Comment (by EPA-Frank Borsuk)

(b) (5)

███

| Christopher Hunter | I no longer think I'll ever be done. But thanks, I'll... | 01/03/2011 01:26:29 PM |

From: Christopher Hunter/DC/USEPA/US
To: Stefania Shamet/R3/USEPA/US@EPA
Date: 01/03/2011 01:26 PM
Subject: Re: JUST WHEN YOU THINK YOU'RE DONE WITH THE PD COMMENTS ...Fw: Addition to the PD #13 concerning No Effect on Birds Comment (by EPA-Frank Borsuk)

I no longer think I'll ever be done. But thanks, I'll incorporate this.

| Stefania Shamet | ----- Forwarded by Stefania Shamet/R3/USEPA/... | 01/03/2011 01:22:16 PM |

From: Stefania Shamet/R3/USEPA/US
To: Christopher Hunter/DC/USEPA/US@EPA
Date: 01/03/2011 01:22 PM
Subject: JUST WHEN YOU THINK YOU'RE DONE WITH THE PD COMMENTS ...Fw: Addition to the PD #13 concerning No Effect on Birds Comment (by EPA-Frank Borsuk)

----- Forwarded by Stefania Shamet/R3/USEPA/US on 01/03/2011 01:21 PM -----

From: Frank Borsuk/R3/USEPA/US
To: Stefania Shamet/R3/USEPA/US@EPA
Cc: Matthew Klasen/DC/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA
Date: 01/03/2011 01:13 PM
Subject: Re: Addition to the PD #13 concerning No Effect on Birds Comment (by EPA-Frank Borsuk)

(b) (5)

███

Frank Borsuk, Ph.D.
Aquatic/Fisheries Biologist
Freshwater Biology Team
USEPA-Region 3 (Wheeling Office)
Office of Monitoring & Assessment (3EA50)
Environmental Assessment & Innovation Division
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
304-234-0241 Phone
304-234-0260 Fax
borsuk.frank@epa.gov

Please visit our website at http://epa.gov/reg3esd1/3ea50.htm

Matthew Klasen/DC/USEPA/US	To	Stefania Shamet	
01/03/2011 02:02 PM	cc		
	bcc		
	Subject	Re: 52A -- this look right?	

No, we should be OK. I've been making incremental formatting edits since yesterday to the doc, so I'm going to view side by side and make your changes when they come in.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Stefania Shamet	Does this create a version control issue? I'm ab...	01/03/2011 02:01:33 PM

From: Stefania Shamet/R3/USEPA/US
To: Matthew Klasen/DC/USEPA/US@EPA
Date: 01/03/2011 02:01 PM
Subject: Re: 52A -- this look right?

Does this create a version control issue? I'm about to send edits to 1-67 (in about 15 min) in redline.

Matthew Klasen	Should be all set -- I already added it in. -----------...	01/03/2011 01:59:19 PM

From: Matthew Klasen/DC/USEPA/US
To: Stefania Shamet/R3/USEPA/US@EPA
Date: 01/03/2011 01:59 PM
Subject: Re: 52A -- this look right?

Should be all set -- I already added it in.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Stefania Shamet	I thought 22 was sufficient, but your answer look...	01/03/2011 01:58:47 PM

From: Stefania Shamet/R3/USEPA/US
To: Matthew Klasen/DC/USEPA/US@EPA
Date: 01/03/2011 01:58 PM
Subject: Re: 52A -- this look right?

I thought 22 was sufficient, but your answer looks fine. I'm about to send 1-67. WAnt me to incorporate it?

Matthew Klasen	Hey Stef: Chris pointed out after sending cross-r...	01/03/2011 01:55:43 PM

From: Matthew Klasen/DC/USEPA/US
To: Stefania Shamet/R3/USEPA/US@EPA
Cc: Christopher Hunter/DC/USEPA/US@EPA

Hey Stef:

Chris pointed out after sending cross-references that we don't have great cross-references for 52A (an "old" comment regarding Se and Seng Camp).

I took a shot at writing up a paragraph to directly respond. Does this seem OK?

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

(b) (5)

Stefania Shamet/R3/USEPA/US

01/03/2011 02:35 PM

To	Matthew Klasen
cc	
bcc	
Subject	1A-67A -- WOULD HELP IF I ATTACH!

May or may not be on the 3pm call.

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responsessds.docx

To Marcel Tchaou

cc

bcc

Subject Fw: JUST WHEN YOU THINK YOU'RE DONE WITH THE
PD COMMENTS ...Fw: Addition to the PD #13 concerning No
Effect on Birds Comment (by EPA-Frank Borsuk)

Some more references

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov
----- Forwarded by Christopher Hunter/DC/USEPA/US on 01/03/2011 03:12 PM -----

From:	Stefania Shamet/R3/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Date:	01/03/2011 01:22 PM
Subject:	JUST WHEN YOU THINK YOU'RE DONE WITH THE PD COMMENTS ...Fw: Addition to the PD #13 concerning No Effect on Birds Comment (by EPA-Frank Borsuk)

----- Forwarded by Stefania Shamet/R3/USEPA/US on 01/03/2011 01:21 PM -----

From:	Frank Borsuk/R3/USEPA/US
To:	Stefania Shamet/R3/USEPA/US@EPA
Cc:	Matthew Klasen/DC/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA
Date:	01/03/2011 01:13 PM
Subject:	Re: Addition to the PD #13 concerning No Effect on Birds Comment (by EPA-Frank Borsuk)

Stef/Matt:

FYI - An addition to the PD Question/Response #13 response concerning other water fowl. This information is taken from:

USFWS 2005. Public comment package in response to the U.S. Environmental Protection Agency's (EPA) request for scientific information, data, and views pertaining to the "*Draft Aquatic Life Criteria Document for Selenium* " (Federal Register 69(242):75541-75546; December 17, 2004).

I will forward this entire USFWS doc to you as a separate email.

Frank

(b) (5)

(b) (5)

Frank Borsuk, Ph.D.
Aquatic/Fisheries Biologist
Freshwater Biology Team
USEPA-Region 3 (Wheeling Office)
Office of Monitoring & Assessment (3EA50)
Environmental Assessment & Innovation Division
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
304-234-0241 Phone
304-234-0260 Fax
borsuk.frank@epa.gov

Please visit our website at http://epa.gov/reg3esd1/3ea50.htm

Frank Borsuk/R3/USEPA/US
01/03/2011 04:41 PM

To Stefania Shamet, Margaret Passmore, borsuk.frank, John Forren

cc David Rider

bcc

Subject Initial Response from Frank (Need DMR records review from Dave Rider)-- Fw: More Spruce

My comments are in light blue. I will work with Dave Ride rot confirm the DMR records.

Frank

Frank Borsuk, Ph.D.
Aquatic/Fisheries Biologist
Freshwater Biology Team
USEPA-Region 3 (Wheeling Office)
Office of Monitoring & Assessment (3EA50)
Environmental Assessment & Innovation Division
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
304-234-0241 Phone
304-234-0260 Fax
borsuk.frank@epa.gov

Please visit our website at http://epa.gov/reg3esd1/3ea50.htm

----- Forwarded by Frank Borsuk/R3/USEPA/US on 01/03/2011 03:13 PM -----

From: Stefania Shamet/R3/USEPA/US

To: Frank Borsuk/R3/USEPA/US@EPA

Cc: Margaret Passmore/R3/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA

Date: 01/03/2011 02:28 PM

Subject: More Spruce

Frank -- I think we still need some kind of response to the following. Can you provide? I know you asked about the S or U on the SMCRA permit. I think Greg or Maggie have the actual comments; it might be there:

(b) (5)

Response #30A – RESPONSE COMING – TECHNICAL REVIEW

(b) (5)

(b) (5)

(b) (5)

Julia McCarthy/R8/USEPA/US
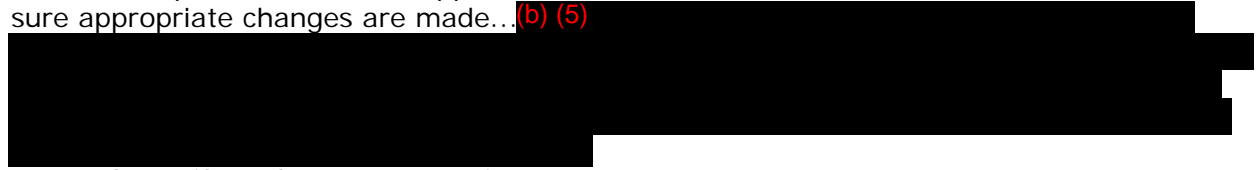
01/03/2011 05:04 PM

To Christopher Hunter

cc

bcc

Subject Appendix 2 Edits

Hey Chris,
Here's the updated version of Appendix 2. I still have to cross check with the FD to make sure appropriate changes are made… (b) (5)

Let me know if you have any questions!
Cheers,
Julia

Julia McCarthy (on detail)
Life/Environmental Scientist
U.S. Environmental Protection Agency
Office of Wetlands, Oceans and Watersheds
Wetlands Division
Washington, DC
(202) 566-1660
mccarthy.julia@epa.gov

Success is like wrestling a gorilla. You don't quit when you're tired. You quit when the

gorilla is tired. ~Robert Strauss [ ] - Appendix 2 macroinvertebrates 010311.doc

ATTACHMENT REDACTED – DELIBERATIVE

To   Frank Borsuk

cc   Stefania Shamet, Margaret Passmore, John Forren

bcc

Subject   updated DMRs for WV1017021

Frank,

Here is the digest of the latest available DMRs. September 30th, which I received last week from WVDEP. Very quick service as I requested it after 4 pm and received it just after 5 pm.

Stef's response to 29 covers the complaint that Dal Tex discharges don't reflect potential for Spruce selenium elevations.

I will be in the group with MIRA starting at 8:30 tomorrow so we should talk before that.

Dave

David E. Rider
US Environmental Protection Agency
1650 Arch Street (3EA50)
Philadelphia, PA 19103-2029
215-814-2787

Learn more about the Office of Monitoring & Assessment at http://epa.gov/reg3esd1/3ea50.htm

ATTACHMENT REDACTED – DELIBERATIVE

Se Trends to 9-30-10.xlsx

Matthew Klasen/DC/USEPA/US

01/03/2011 06:04 PM

To Kevin Minoli

cc Stefania Shamet, Christopher Hunter, Gregory Peck, Karyn Wendelowski

bcc

Subject RD responses 1A-67A for your review

Hi Kevin,

Here are RD comment responses #1A-67A for you to begin your long RD comment review. Huge thanks to everyone who helped pull these together.

A few notes:
- The header explains the highlighting scheme, but to reiterate here: Yellow highlighted comments mean comments are new; non-highlighted comments can be answered with just a PD cross-reference. We'll remove the highlighting before we finalize the document.

- There are three responses not yet ready for your review, which we've **highlighted in teal**:
  - **14A** (materials handling);
  - **30A** (outfall 015 and underground mining); and
  - **67A** (selenium assumptions).
  The remaining 64 responses should be good to go.

- We know that some of these comments/responses will require changes to the FD, and Chris will be working to make those changes concurrently with your review.

Let us know tomorrow how your review is progressing so that we can be ready with the next chunk.

And for context, there are four main chunks of RD comments: **1A-67A** (this batch), **68A-242A** (mostly conductivity issues), **243A-307A** (mitigation), and **1B-39B** (WVDEP comments).

Let me know if you have any questions.

Thanks,
Matt

                              `ATTACHMENT REDACTED - DELIBERATIVE`

2011-01-03 RD 1A-67A for Kevin's review.docx

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Matthew
Klasen/DC/USEPA/US

01/04/2011 01:19 AM

To   Matthew Klasen

cc

bcc

Subject   stuff

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780

cell (202) 380-7229 ⬜ - 2011-01-03 Compiled H&W RD Comment Responses.docx ⬜ -
2011-01-04 Draft Spruce Q&As.doc

ATTACHMENT REDACTED – DELIBERATIVE

Christopher Hunter/DC/USEPA/US

01/04/2011 07:41 AM

To Ross Geredien

cc

bcc

Subject Re: Tomorrow's briefing with Pete

Ross

When you get in, can you print 12 copies of these docs and staple them together for the briefing? Thanks

1-04-11 Briefing Agenda.docx Spruce Site Map.docx TABLE OF CONTENTS.docx   Document Withheld-FOIA (b)(5)

Document Withheld-FOIA (b)(5)

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Ross Geredien	Sure	01/04/2011 07:31:09 AM

| From:	Ross Geredien/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Cc:	"Julia McCarthy" <McCarthy.Julia@epamail.epa.gov>, "Ross Geredien" <Geredien.Ross@epamail.epa.gov>
Date:	01/04/2011 07:31 AM
Subject:	Re: Tomorrow's briefing with Pete

Sure

Ross Geredien
ORISE Fellow
EPA Office of Wetlands, Oceans, and Watersheds
202-566-1466
Geredien.ross(AT)epa.gov

-----Christopher Hunter/DC/USEPA/US wrote: -----

=======================
To: "Julia McCarthy" <McCarthy.Julia@epamail.epa.gov>, "Ross Geredien" <Geredien.Ross@epamail.epa.gov>
From: Christopher Hunter/DC/USEPA/US
Date: 01/03/2011 07:06PM
Subject: Tomorrow's briefing with Pete
=======================
    Since you've both been so key in reviewing and drafting, I'd like if you could attend the 9:30am briefing on Spruce in Pete's conference room. Thanks for all your help.
Chris Hunter
US EPA, Wetlands Protection Division
(202) 566-1454 (t)
(202) 573-6478 (c)
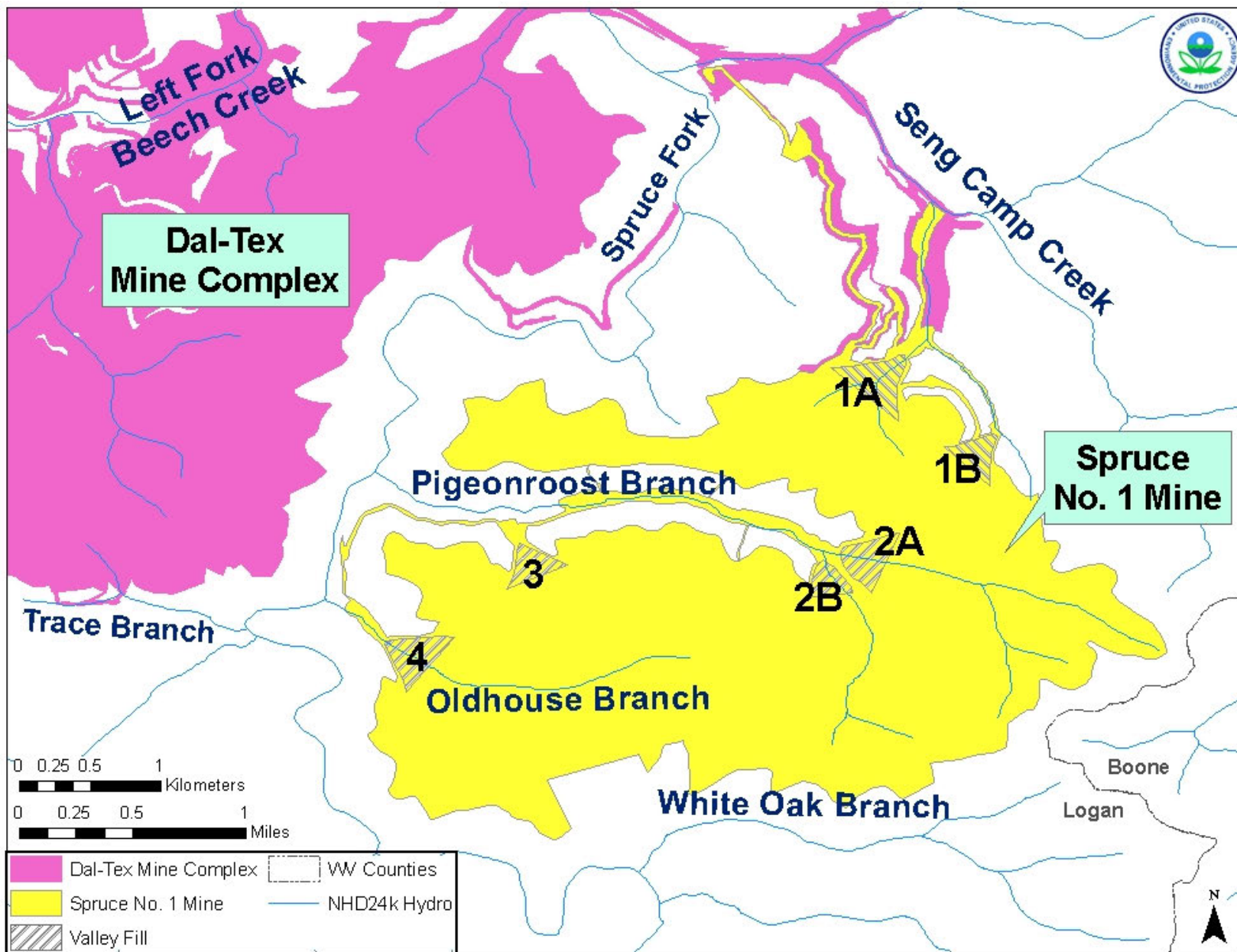
Jim Pendergast/DC/USEPA/US 01/04/2011 08:40 AM	To	Christopher Hunter, David Evans, Brian Frazer, Palmer Hough
	cc	
	bcc	
	Subject	Re: Daily Spruce Update

(b) (5)

ATTACHMENT REDACTED – DELIBERATIVE

2010-12-29 Draft Spruce Release v.2 JFP.docx

Christopher Hunter	Attached is the last draft of the press release I h...	01/03/2011 07:11:37 PM

From: Christopher Hunter/DC/USEPA/US
To: Denise Keehner/DC/USEPA/US@EPA
Cc: David Evans/DC/USEPA/US@EPA, Jim Pendergast/DC/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA, Nancy Stoner/DC/USEPA/US@EPA, Peter Silva/DC/USEPA/US@EPA
Date: 01/03/2011 07:11 PM
Subject: Re: Daily Spruce Update

Attached is the last draft of the press release I have seen. This was forwarded to Betsaida on 12/29. She asked some follow-up questions on jobs, but I haven't seen any further emails on the release.

Please let me know if you have any other questions.
Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov
-----Denise Keehner/DC/USEPA/US wrote: -----

To: Christopher Hunter/DC/USEPA/US@EPA
From: Denise Keehner/DC/USEPA/US
Date: 01/03/2011 06:24PM
Cc: David Evans/DC/USEPA/US@EPA, Jim Pendergast/DC/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA, Nancy Stoner/DC/USEPA/US@EPA, Peter Silva/DC/USEPA/US@EPA
Subject: Re: Daily Spruce Update

Chris--This is very helpful and nice to be able to provide to Nancy and Pete. Speaking of Pete and Nancy, please forward the latest draft of the Press Release (and info on whether it is with Betsaida or not) to Nancy Stoner and Pete ASAP. I have a hardcopy of what I think is the latest that Tanya provided to me earlier today--but I don't seem to have the electronic version or I would have sent it myself. Thanks for all your attention to the details here and your continuing hard work on this.

Christopher Hunter---01/03/2011 05:08:41 PM---Hi Denise, here is today's update on the Final Determination. A lot of progress has been made on dra

From: Christopher Hunter/DC/USEPA/US

To: Denise Keehner/DC/USEPA/US@EPA

Cc: David Evans/DC/USEPA/US@EPA, Jim Pendergast/DC/USEPA/US@EPA, Palmer
Hough/DC/USEPA/US@EPA

Date: 01/03/2011 05:08 PM

Subject: Daily Spruce Update

Hi Denise,
here is today's update on the Final Determination. A lot of progress has been made on drafting responses, we're now primarily occupied with reviewing and ensuring that significant responses are folded back into the main document.

Spruce FD Document -- The latest draft was sent to AA's and AO on 12/30, as promised. We asked for comments back on the draft by COB 1/6, and any comments and the critical RD Responses to Comments will be incorporated before COB 1/10.

Spruce FD Appendices -- essentially reviewed and finalized, with the exception of new critical RD "Response to Comments". Any final relevant responses to comments will need to be incorporated into other appendices.

PD Response to Comments -- compiled and finalized. Sent to OW for incorporation and cross-referencing to other comments in the master response to comments appendix.

RD Response to Comments :

Drafting new HW responses -- Approximately 90% drafted. Sections of responses are now being reviewed by OGC and other program staff. Target date is Wednesday for comments and review before final responses are compiled.
WVDEP comments & Response to Corps 9/09 letter -- R3 reviewing and responding

Briefings -
AAOW - 1/4, 9:30-10:30
AO - 1/5, 1:00-1:45

Communications Materials:

Draft press release -- sent to OA 12/28, revised draft circulated 12/29.
Q&As -- Partially complete. MK to continue developing.
Website - Chris H. to draft by 1/5 for review.

Spruce FR Notice -- MK to draft following completion of responses to comments.

[attachment "2010 12 29 Draft Spruce Release v 2 docx" deleted by J m Pendergas/DC USEPA US]

Frank Borsuk/R3/USEPA/US

01/04/2011 09:54 AM

To   Stefania Shamet
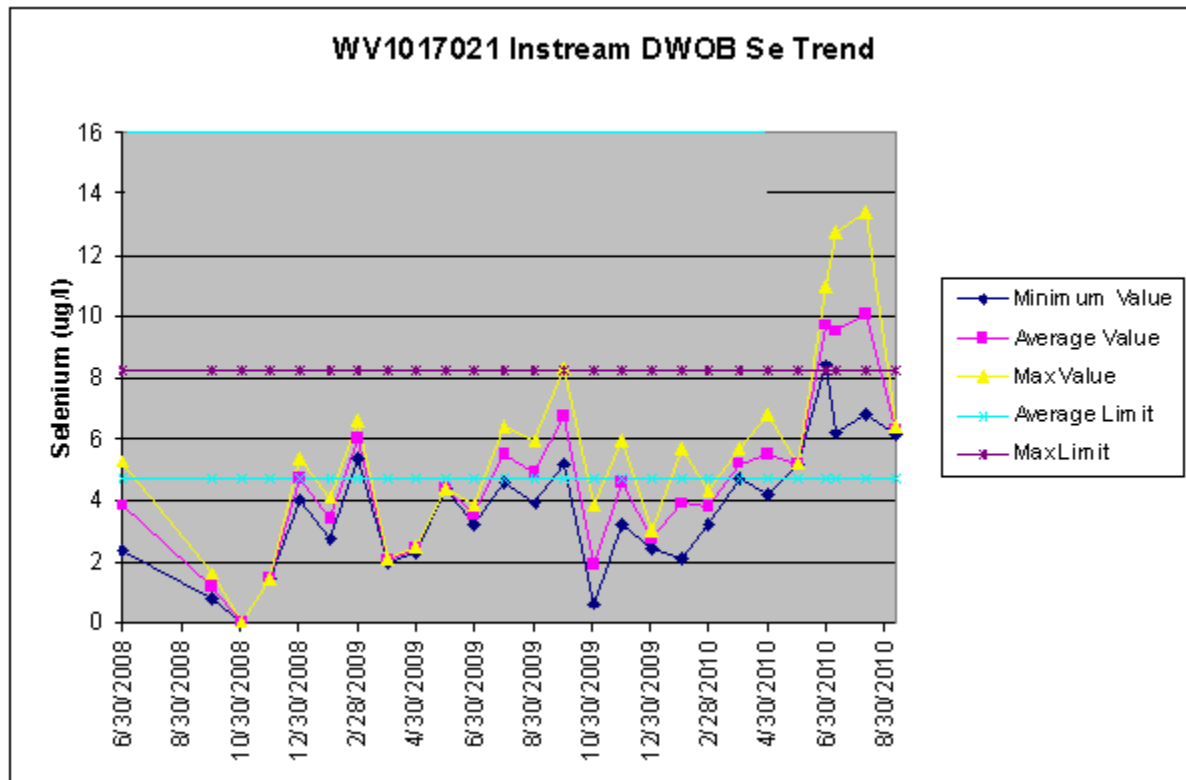
cc   Margaret Passmore, David Rider, John Forren, borsuk.frank

bcc

Subject   Stef - New Issue with Selenium on White Oak Branch

(b)
(5)

WV1017021 Instream DWOB Se Trend

(b) (5)

(b) (5)

Frank Borsuk, Ph.D.
Aquatic/Fisheries Biologist
Freshwater Biology Team
USEPA-Region 3 (Wheeling Office)
Office of Monitoring & Assessment (3EA50)
Environmental Assessment & Innovation Division
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
304-234-0241 Phone
304-234-0260 Fax
borsuk.frank@epa.gov

Please visit our website at http://epa.gov/reg3esd1/3ea50.htm

Christopher Hunter/DC/USEPA/US

01/04/2011 11:51 AM

To   Ann Campbell, Jordan Dorfman

cc   Tanya Code

bcc

Subject   Briefing Materials for 1-5-11 meeting on Spruce

Here are the relevant materials; agenda, map of the Spruce site, and current structure/table of contents for the Final Determination. Please let me know if you need anything else.

Thanks

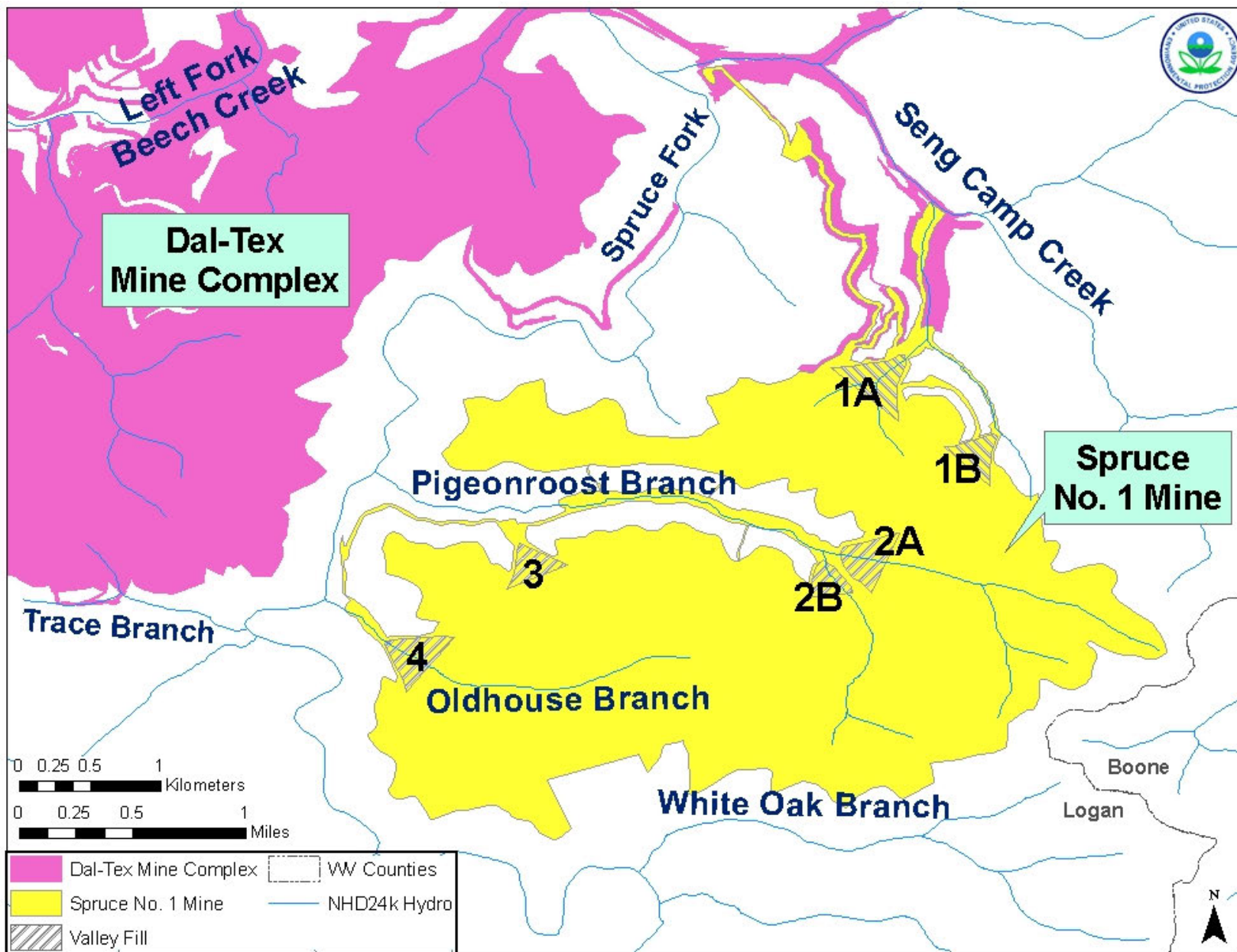📄   📄   📄   `Document Withheld-FOIA (b)(5)`

1-05-11 Briefing Agenda.docx   Spruce Site Map.docx   TABLE OF CONTENTS.docx

`Document Withheld-FOIA (b)(5)`

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Here are the current drafts of RD comments:

Document #1: H&W RD Comments (1A-307A)
1A-67A are nearly complete, except for three questions that still need work (14A, 30A, 67A). Kevin is reviewing now and will have comments this afternoon.
67A-242A and **243-307** still await R3 updates, coming this afternoon.
243A-307A are in OWOW (Palmer, Brian T., Chris) for updates.

ATTACHMENT REDACTED – DELIBERATIVE

2011-01-03a Compiled H&W RD Comment Responses.docx

Document #2: WVDEP Responses
1B-38B are teed up for Kevin's review this afternoon.

ATTACHMENT REDACTED – DELIBERATIVE

2011-01-04 Compiled WVDEP RD Comment Responses.doc

Let me know if you have any questions. In terms of process, 1A-67A and 1B-38B are further along, so those may be better for you and Denise to review first (both so they're more polished for your review, and so that we can finalize those sections more quickly.

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

| Tanya Code | Denise would like to read through. Also - I'll be s... | 01/04/2011 11:13:27 AM |

From:	Tanya Code/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA
Date:	01/04/2011 11:13 AM
Subject:	Can you send me & Denise the most recent verison of the response to comments from HW? Thx.

Denise would like to read through. Also - I'll be setting up a meeting for late Wed to discuss, per discussion at OWOW staff meeting yesterday (hopefully Dave and Jim relayed msg)

Thanks,

Tanya Code
Special Assistant
Office of Wetlands, Oceans and Watersheds

U.S. Environmental Protection Agency
Tel: 202.566.1063
Fax: 202.566.1147

Here ya go! And I corrected the year... get with it, man, it's 2011.

ATTACHMENT REDACTED - DELIBERATIVE

Spruce FD 010311 draft.doc

Julia McCarthy
on detail to USEPA Headquarters
Office of Wetlands, Oceans and Watersheds
(202) 566-1660
mccarthy.julia@epa.gov

A land ethic, then, reflects the existence of an ecological conscience, and this in turn reflects a connection of individual responsibility for the health of the land. Health is the capacity of the land for self-renewal. Conservation is our effort to understand and preserve this capacity. ~Aldo Leopold

Matthew Klasen/DC/USEPA/US

01/04/2011 02:50 PM

To   Kevin Minoli

cc   Christopher Hunter, Gregory Peck, Karyn Wendelowski, Stefania Shamet

bcc

Subject   Re: RD responses 1A-67A for your review

Great, thanks! I'll send you the next batch (WVDEP) in a few minutes.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Kevin Minoli	Matt- Attached are my comments on the first bat...	01/04/2011 02:37:33 PM

From: Kevin Minoli/DC/USEPA/US
To: Matthew Klasen/DC/USEPA/US@EPA
Cc: Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date: 01/04/2011 02:37 PM
Subject: Re: RD responses 1A-67A for your review

Matt- Attached are my comments on the first batch. Obviously a tremendous amount of work has gone into crafting these responses and for the most part my suggestions are pretty easy to incorporate. (b)(5) Attorney-Client Privelige

Thanks, Kevin

[attachment "2011-01-03 RD 1A-67A for Kevin's review.ksm.docx" deleted by Matthew Klasen/DC/USEPA/US]

| Matthew Klasen | Hi Kevin, Here are RD comment responses #1A-... | 01/03/2011 06:04:50 PM |

From:	Matthew Klasen/DC/USEPA/US
To:	Kevin Minoli/DC/USEPA/US@EPA
Cc:	Stefania Shamet/R3/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA
Date:	01/03/2011 06:04 PM
Subject:	RD responses 1A-67A for your review

Hi Kevin,

Here are RD comment responses #1A-67A for you to begin your long RD comment review. Huge thanks to everyone who helped pull these together.

A few notes:
- The header explains the highlighting scheme, but to reiterate here: Yellow highlighted comments mean comments are new; non-highlighted comments can be answered with just a PD cross-reference. We'll remove the highlighting before we finalize the document.

- There are three responses not yet ready for your review, which we've **highlighted in teal**:
    - **14A** (materials handling);
    - **30A** (outfall 015 and underground mining); and
    - **67A** (selenium assumptions).
    The remaining 64 responses should be good to go.

- We know that some of these comments/responses will require changes to the FD, and Chris will be working to make those changes concurrently with your review.

Let us know tomorrow how your review is progressing so that we can be ready with the next chunk.

And for context, there are four main chunks of RD comments: **1A-67A** (this batch), **68A-242A** (mostly conductivity issues), **243A-307A** (mitigation), and **1B-39B** (WVDEP comments).

Let me know if you have any questions.

Thanks,
Matt

[attachment "2011-01-03 RD 1A-67A for Kevin's review.docx" deleted by Kevin Minoli/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780

cell (202) 380-7229

Matthew Klasen/DC/USEPA/US	To	Tanya Code
	cc	Christopher Hunter
01/04/2011 03:18 PM	bcc	
	Subject	Fw: RD responses 1A-67A for your review

Hey Tanya,

If you and Denise haven't started reviewing the WVDEP comments on the RD (#1B-38B -- the second attachment I sent you earlier), go ahead and use this updated version. I just sent these to Kevin for his review, after making some edits that Chris recommended.

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/04/2011 03:17 PM -----

From:	Matthew Klasen/DC/USEPA/US
To:	Kevin Minoli/DC/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/04/2011 03:07 PM
Subject:	Re: RD responses 1A-67A for your review

Hi Kevin,

Here's the next batch for you: WVDEP comments 1B-38B. Chris flagged one legal sentence (highlighted) in the response to 2B that may no longer be in the FD. This may be worth just deleting.

Other than that, all of these responses should be ready for your review. We'll work to get you another subset of these to look at hopefully by COB today, which should be 68A-110A or so. Let us know your progress this afternoon on these.

Thanks,
Matt

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-04 Compiled WVDEP RD Comment Responses.doc

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Kevin Minoli	Matt- Attached are my comments on the first bat...	01/04/2011 02:37:33 PM

From:	Kevin Minoli/DC/USEPA/US

To:	Matthew Klasen/DC/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/04/2011 02:37 PM
Subject:	Re: RD responses 1A-67A for your review

Matt- Attached are my comments on the first batch. Obviously a tremendous amount of work has gone into crafting these responses and for the most part my suggestions are pretty easy to incorporate. (b) (5) Att orn ey- Clie nt Priv elig e

- ▪

- ▪

Thanks, Kevin

[attachment "2011-01-03 RD 1A-67A for Kevin's review.ksm.docx" deleted by Matthew Klasen/DC/USEPA/US]

| Matthew Klasen | Hi Kevin, Here are RD comment responses #1A-... | 01/03/2011 06:04:50 PM |

From:	Matthew Klasen/DC/USEPA/US
To:	Kevin Minoli/DC/USEPA/US@EPA
Cc:	Stefania Shamet/R3/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA
Date:	01/03/2011 06:04 PM
Subject:	RD responses 1A-67A for your review

Hi Kevin,

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    - **14A** (materials handling);
    - **30A** (outfall 015 and underground mining); and
    - **67A** (selenium assumptions).
    The remaining 64 responses should be good to go.

- We know that some of these comments/responses will require changes to the FD, and Chris will be working to make those changes concurrently with your review.

Let us know tomorrow how your review is progressing so that we can be ready with the next chunk.

And for context, there are four main chunks of RD comments: **1A-67A** (this batch), **68A-242A** (mostly conductivity issues), **243A-307A** (mitigation), and **1B-39B** (WVDEP comments).

Let me know if you have any questions.

Thanks,
Matt

[attachment "2011-01-03 RD 1A-67A for Kevin's review.docx" deleted by Kevin Minoli/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Matthew Klasen/DC/USEPA/US	To	Christopher Hunter	
01/04/2011 03:36 PM	cc		
	bcc		
	Subject	Fw: RD comments 68-242	

Here's what Stef just sent -- so just worry about 68-113A for now. Also, ignore the strikethroughs; I'm going to leave those in the final version with appropriate cross-refs (unless they're simply factual statements and we just say "comment noted.")

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/04/2011 03:34 PM -----

From:	Stefania Shamet/R3/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Date:	01/04/2011 02:26 PM
Subject:	RD comments 68-242

(b) (5)

Still optimistic that I can get you the rest by tomorrow am.

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responsessds.docx

Christopher Hunter/DC/USEPA/US

01/04/2011 03:54 PM

To Marcel Tchaou

cc

bcc

Subject Selenium comments and responses

Marcel,
here is what I've seen so far from the Region. These aren't complete yet, but they should give you a better idea of the direction the region is going. (b) (5)

Chris

ATTACHMENT REDACTED - DELIBERATIVE

Selenium responses.docx

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

To   Bob Sussman, Gregory Peck, Stan Meiburg

cc   Amy Caprio, Michael DAndrea

bcc

Subject   Region III DRAFT Response to WV/VA Guidance

As requested during the MTM conference call this morning attached are several documents related to the WV and VA mining guidance. The first two attachments below are DRAFT responses to VA and WV. We are in the process of coordinating with HQ with regard to these letters and the text of the two letters is likely to change. The third document is the response Region III initially sent upon receipt of the WV guidance. The final attachment is the response Region III received from WV in response to our initial letter regarding the WV guidance.

Thanks.

bill e.

William C. Early
Deputy Regional Administrator
Middle Atlantic Region
U. S. Environmental Protection Agency
215 814 2626
215 814 2901 (Fax)
Early.William@epa.gov

--

    WORD ATTACHMENTS REDACTED - DELIBERATIVE

[DRAFT]l2davisreguidance.docx   [DRAFT]l2huffmanresopnse1019ltr.docx   WVGuidance10810final.PDF

Shawn Garvin 10-19-10 re Narrative WQS.pdf

OCT 0 8 2010

The Honorable Randy C. Huffman
Secretary
Department of Environmental Protection
601-57th Street
Charleston, West Virginia 25304

Dear Secretary Huffman:

The U.S. Environmental Protection Agency Region III (EPA) received a copy of the West Virginia Department of Environmental Protection's (WVDEP) *Permitting Guidance for Surface Coal Mining Operations to Protect West Virginia's Narrative Water Quality Standards, 47 CSR 2 §§ 3.2.e and 3.2.i* (West Virginia Guidance) and the accompanying justification and background document (Justification document).

EPA agrees that the reasonable potential of discharges from surface coal mining operations to cause or contribute to violations of water quality standards should be considered and addressed as part of the National Pollutant Discharge Elimination System (NPDES) permitting process. EPA staff are continuing to review the West Virginia Guidance and the Justification document. Our initial review of these documents has raised a number of questions that touch on the scientific conclusions and policy or legal statements in the document.
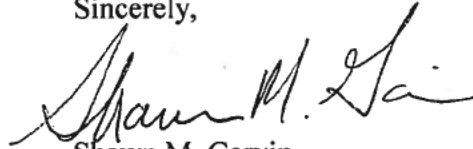
Accordingly, I am proposing that a meeting be scheduled between EPA and West Virginia technical staff to discuss the West Virginia Guidance and the Justification document. We envision such a meeting to include staff from our agencies' respective NPDES and water quality standards and assessment programs, as well as biologists from both agencies. Such a meeting would give EPA staff an opportunity to ask questions and raise concerns and WVDEP staff an opportunity to provide clarification. We will be in contact shortly at the appropriate staff levels to schedule a meeting.

In the interim, EPA's NPDES and water quality staff will continue to work with your staff to review NPDES permits and water quality issues. As you are aware, on April 1, 2010, EPA released interim final guidance to the Regional offices titled: *Guidance on Improving EPA Review of Appalachian Surface Coal Mining Operations under the Clean Water Act, National Environmental Policy Act, and the Environmental Justice Executive Order* (SCM Guidance). EPA continues to view the SCM Guidance as providing clarification of requirements established under the Clean Water Act and implementing regulations for the EPA Regions in reviewing permits for discharges associated with Appalachian surface coal mining projects.

We look forward to continuing to work with you and your staff to protect West Virginia's waters and will contact WVDEP shortly to arrange a meeting. Please do not hesitate to contact me or have your staff contact Mrs. Jessica Greathouse, EPA's West Virginia Liaison, at 304-234-0275 if you wish to discuss this matter further.

Sincerely,

Shawn M. Garvin
Regional Administrator

October 19, 2010

Shawn M. Garvin, Regional Administrator
U. S. EPA, Region III (3RA00)
1650 Arch Street
Philadelphia, PA   19103-2029

Dear Mr. Garvin: *Re: Response to October 8, 2010 Letter*

Thank you for your letter of October 8, 2010 acknowledging the Environmental Protection Agency's ("EPA") receipt of the West Virginia Department of Environmental Protection's ("WVDEP") Permitting Guidance for Surface Coal Mining Operations to Protect West Virginia's Narrative Water Quality Standards and the accompanying justification and background document. I understand from your letter that EPA is still in the process of reviewing the aforementioned documents, but that your initial review has raised policy, legal, and scientific issues that EPA would like to discuss with WVDEP. I appreciate the opportunity to discuss these issues and agree that a meeting between our agencies would be productive. I believe, however, that a meeting between EPA and WVDEP technical staff would be premature at this point, until we have sufficiently addressed the policy and legal questions that EPA may have.

Accordingly, I would prefer a meeting at a higher level involving staff capable of addressing all of these issues, particularly those involving policy or legal matters that are not within the purview of our respective technical staffs. If we can reach some understandings on these broader-scale issues, then the next step might be a meeting of the technical staffs. Please contact me to schedule this meeting at your earliest convenience, or give me your thoughts in response.

I look forward to hearing from you.

Sincerely,

Randy C. Huffman
Cabinet Secretary

RCH/kb

Gregory Peck/DC/USEPA/US	To	Karyn Wendelowski, Kevin Minoli
01/04/2011 04:12 PM	cc	
	bcc	
	Subject	Fw: Region III DRAFT Response to WV/VA Guidance

FYI. (b) (5)

----- Forwarded by Gregory Peck/DC/USEPA/US on 01/04/2011 04:10 PM -----

From:	William Early/R3/USEPA/US
To:	Bob Sussman/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Stan Meiburg/R4/USEPA/US@EPA
Cc:	Amy Caprio/R3/USEPA/US@EPA, Michael DAndrea/R3/USEPA/US@EPA
Date:	01/04/2011 04:08 PM
Subject:	Region III DRAFT Response to WV/VA Guidance

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Thanks.

bill e.

William C. Early
Deputy Regional Administrator
Middle Atlantic Region
U. S. Environmental Protection Agency
215 814 2626
215 814 2901 (Fax)
Early.William@epa.gov
--

Document Withheld-FOIA(b)(5) Document Withheld-FOIA(b)(5)

[DRAFT]l2davisreguidance.docx   [DRAFT]l2huffmanresopnse1019ltr.docx   WVGuidance10810final.PDF

Shawn Garvin 10-19-10 re Narrative WQS.pdf

west virginia department of environmental protection

October 19, 2010

Shawn M. Garvin, Regional Administrator
U. S. EPA, Region III (3RA00)
1650 Arch Street
Philadelphia, PA   19103-2029

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I look forward to hearing from you.

Sincerely,

Randy C. Huffman
Cabinet Secretary

RCH/kb

Promoting a healthy environment.

OCT 0 8 2010

The Honorable Randy C. Huffman
Secretary
Department of Environmental Protection
601-57th Street
Charleston, West Virginia 25304

Dear Secretary Huffman:

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Sincerely,

Shawn M. Garvin
Regional Administrator

Laura Bachle/DC/USEPA/US

01/04/2011 04:21 PM

To Brian Frazer

cc

bcc

Subject Laura's files on KCH

Buffalo Mtn Briefingpaper 2-10-10sds.doc Buffalo Mtn one pg_020510.doc KingCoalHwyNEPAOptionsPaperDr05-09jp2.doc

ATTACHMENT REDACTED - DELIBERATIVE

Laura Bachle, AICP
OW - FHWA National Liaison
U.S. EPA

_____

Mailing: Courier:
MC 4502T   1301 Constitution Ave. NW
1200 Pennsylvania Ave. NW   Room7318F
Washington, D.C. 20004   Washington, DC 20469
Direct: (202)566-2468
FAX: (202)566-1349
bb# (202)306-7035
bachle.laura@epa.gov

Gregory Peck/DC/USEPA/US
01/04/2011 04:30 PM

To Lynn Zipf

cc Matthew Klasen

bcc

Subject HELP Spruce selenium response -- need your input on support for the 4 ppm whole body threshold

Hey Lynn

We haven't received any response from Betsy on this request - can you help? Thanks

----- Forwarded by Gregory Peck/DC/USEPA/US on 01/04/2011 04:29 PM -----

From:	Gregory Peck/DC/USEPA/US
To:	Betsy Behl/DC/USEPA/US@EPA, Joe Beaman/DC/USEPA/US@EPA
Cc:	Matthew Klasen/DC/USEPA/US@EPA, Lynn Zipf/DC/USEPA/US@EPA, stoner.nancy@epa.gov, Ephraim King/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Frank Borsuk/R3/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA
Date:	01/02/2011 12:45 PM
Subject:	Spruce selenium response -- need your input on support for the 4 ppm whole body threshold

Betsy and Joe:

Hope you both are enjoying your 2011 so far. Thanks again for your help a couple weeks ago in pulling together some selenium-related responses to comments on the Spruce #1 veto. We're finishing up responses to comments and had one follow-up question for your group related to the state of the science on Se whole-body effect levels.

See forwarded note below from R3 related to one of the comments (#67A -- also pasted below along with the answer you passed along a couple weeks ago). (b) (5)

ur primary goal is to ensure that the number we use in the Spruce context is consistent with EPA's interpretation of the science in the context of the updated Se criterion.

Please give Matt or me a call if you have any questions. We're coming close to the finish line on the Spruce Final Determination and would appreciate a response as soon as you get a chance to review and talk with appropriate folks in your group.

Thanks,
Greg

(b) (5)

To: Stefania Shamet/R3/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA, borsuk.frank@epa.gov
From: Frank Borsuk/R3/USEPA/US
Date: 12/29/2010 11:21AM
Cc: Matthew Klasen/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, David Rider/R3/USEPA/US@EPA, David Kargbo/R3/USEPA/US@EPA
Subject: Response Supplement #67 Selenium - Support for the 4 ppm whole body threshold

Frank Borsuk, Ph.D.
Aquatic/Fisheries Biologist
Freshwater Biology Team
USEPA-Region 3 (Wheeling Office)
Office of Monitoring & Assessment (3EA50)
Environmental Assessment & Innovation Division
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
304-234-0241 Phone
304-234-0260 Fax
borsuk.frank@epa.gov

Please visit our website at http://epa.gov/reg3esd1/3ea50.htm

Hamilton_2003.pdf   Peterson et al 2009 selenium.pdf

How Might Selenium Moderate the Toxic Effects of Mercury in Stream Fish of the Western U.S.?

SPENCER A PETERSON,*,†
NICHOLAS V.C. RALSTON,‡
DAVID V PECK,† JOHN VAN SICKLE,†
J. DAVID ROBERTSON,§
VICKIE L. SPATE,§ AND
J. STEVEN MORRIS§

National Health and Environmental Effects Research Laboratory, Western Ecology Division, U.S. Environmental Protection Agency, Corvallis, Oregon 97333, Energy and Environmental Research Center, University of North Dakota, 15 North 23rd Street, Stop 9018, Grand Forks, North Dakota 58202-9018, and Department of Chemistry and Research Reactor, Room 209A, University of Missouri, Research Park Drive, Columbia, Missouri 65211

The ability of selenium (Se) to moderate mercury (Hg) toxicity is well established in the literature. Mercury exposures that might otherwise produce toxic effects are counteracted by Se, particularly when Se:Hg molar ratios approach or exceed 1. We analyzed whole body Se and Hg concentrations in 468 fish representing 40 species from 137 sites across 12 western U.S. states. The fish samples were evaluated relative to a published wildlife protective Hg threshold (0.1 μg Hg·g^{-1} wet wt.), the current tissue based methylmercury (MeHg) water quality criterion (WQC) for the protection of humans (0.3 μg Hg·g^{-1} wet wt.) and to presumed protections against Hg toxicity when Se:Hg molar ratios are >1. A large proportion (56%) of our total fish sample exceeded the wildlife Hg threshold, whereas a smaller, but significant proportion (12%), exceeded the MeHg WQC. However, 97.5% of the total fish sample contained more Se than Hg (molar ratio >1) leaving only 2.5% with Se:Hg ratios <1. All but one of the fish with Se:Hg <1, were of the genus *Ptychochelius* (pikeminnow). Scientific literature on Se counteracting Hg toxicity and our finding that 97.5% of the freshwater fish in our survey have sufficient Se to potentially protect them and their consumers against Hg toxicity suggests that Se in fish tissue (Se:Hg molar ratio) must be considered when assessing the potential toxic effects of Hg.

Introduction

Selenium is an essential nutrient for all life forms that have nervous systems, but Se can be toxic when present at high levels in the environment. There is no physiological requirement for Hg, but it bioaccumulates in the aquatic food chain and fish are the chief exposure route for wildlife and humans. In fish, MeHg constitutes 95–97% of the total Hg in fish filets (*1*). Therefore, since total Hg is more easily measured in fish tissue, total Hg measurements are recommended for fish surveys by EPA (*2*).

At high exposures, Se and Hg can each be individually toxic, but evidence supports the 1971 observation by Parizek et al. (*3*) that co-occurring Se and Hg antagonistically reduce each other's toxic effects. In 1972, Ganther et al. (*4*) found that tuna containing an ~1:1 molar ratio of Se:Hg reduced toxic effects of MeHg. He attributed the reduced toxicity to Se in the tuna. Various hypotheses for the Se protective mechanism have been proposed (*5, 6*). One of the most comprehensive involves formation of highly stable organic MeHg-selenocysteine (MeHg-SeCys) that forms in the brain and nervous systems of Hg stressed organisms (*7*). This form and its products are highly stable, thus making the Se biologically unavailable (*8, 9*). Sequestration (deactivation) of Se by high concentrations of MeHg inhibits normal selenoenzyme antioxidant activities that result in the adverse effects associated with Hg toxicity. However, during Hg stress, redistribution of Se from somatic cells and dietary sources to preferentially supply the brain replaces some of the Se lost to HgSe and MeHg-SeCys formation. This reduces the toxic effects by maintaining selenium-dependent enzymes (selenoenzymes) required for brain function and protein synthesis (*10, 11*).

Methylmercury is, by biochemical definition, an irreversible inhibitor of selenoenzymes since it transfers from the thiol of cysteine to the selenol of selenocysteine at the enzymes active site (*7, 12*). Since selenocysteine is a critical component of protein synthesis and must be formed de novo during each cycle of cellular protein synthesis (*7, 12*) inhibition of its formation critically impairs cell metabolism. Based on rat (*7, 13*) and mice studies (*14*), MeHg toxicity appears to occur when molar concentrations of MeHg exceed those of Se and covalent bonding of MeHg to the Se of selenocysteine occurs, thereby irreversibly inhibiting Se-dependent enzymes (*7, 13*). In adult onset, molar surpluses of Se over Hg (Se:Hg molar ratio >1) tend to protect the brains of Hg-stressed organisms. Fetal and young organisms are at much greater risk of toxicity from Hg exposure because the rapid rate of cell division in these organisms requires a steady supply of Se. Watanabe et al. (*14*) demonstrated that in utero Se nutritional status affects MeHg neurotoxicity. Additionally, Ralston et al. (*7*) found that neurofunctional defects (hind leg crossing) can be stabilized, and growth impairments in young rats can be reversed by increasing the amount of Se in their diets, even while maintaining high MeHg exposures.

Peterson et al. (*15*) showed that total Hg (THg) in fish filets exceed that in whole fresh water fish (0.185 μg THg·g^{-1} wet wt. in whole fish = 0.3 μg THg·g^{-1} wet wt. in fish filet). If, as Gather (*4*) suggested, the molar ratio of Se:Hg in fish filet is ~1 it follows that the mass of Se in filet might be approximately the same or greater than that of Hg. Harris et al. (*16*) and Korbas et al. (*17*), recently determined that various forms of Se complex with MeHg in fish filets, making the 95–97% of MeHg in fish tissue (*1*) less toxic to the fish and presumably to consumers (*4*) of the fish than previously thought. Harris et al. (*16*) indicated that zebrafish larvae are 20 times less sensitive to cystine-bound MeHg [MeHg(Cys)], the predominant form of MeHg found in fish tissue, than they are to MeHgCl, that is commonly used in toxicity tests. This was corroborated when Cabañero et al. (*18*) discovered that fish tissue maintains the MeHg(Cys) association after passing through an artificial digestion process. The MeHg(Cys) does not dissociate into toxic MeHg forms as previously suspected.

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Selenium's effect in counteracting Hg toxicity increases throughout Se's nutritionally relevant range and has been demonstrated in all insect, fish, bird, and mammal species tested to date (*13*). However, effects remain controversial. A review of adult effects resulting from fetal exposure in MeHg exposed animal models by Newland et al. (*6*) suggests that diets rich in Se do not uniformly protect against MeHg's effects. The review by Yang et al. (*5*) points out that "a large number of scientific studies have provided strong evidence of the protective role of Se in preventing the detrimental effect of CH_3Hg^+." Ralston et al. (*7*) found that MeHg toxicity in rats could not be predicted from tissue MeHg content alone, but that toxicity was directly related to the Hg:Se molar ratios in the tissue. Thus, it appears that selenium-dependent protection against Hg-toxicity depends not on Hg concentrations per se, but rather on the total mass ratio of Se to Hg. Ganther (*4*) first mentioned the Se:Hg molar ratio of 1:1 as protective against Hg toxicity in fish. Luten et al. (*19*) drew a similar conclusion relative to both freshwater and marine fish.

Since the evidence indicates that Se:Hg molar ratios influence the toxicity of either element and that these ratios are useful in interpretation of toxicity, we developed the fish tissue data in this paper from that perspective. The purpose of this paper is to describe the Se:Hg molar ratios in whole stream fish ($n = 468$) collected from 137 sites across 12 western U.S. states and to relate those ratios to a published wildlife methylmercury (MeHg) consumption threshold (0.1 μg Hg·g^{-1} wet wt.) (*20*). In addition, we comment on these molar ratios relative to the current methylmercury (MeHg) water quality criterion (WQC) for protection of humans (0.3 μg Hg·g^{-1} wet wt.) (*21*) and on potential fish tissue Se toxicity.

Materials and Methods

Procedures for sample site selection, Hg analysis, Hg quality assurance, and quality control (QA/QC), and results of fish tissue Hg analyses were reported previously (*15*). Each is described briefly as follows.

Probability Sample Design. For Se analysis, we selected 468 freeze-dried samples that previously had been analyzed for Hg (*15*). All piscivores ($n = 206$) were analyzed, since those fish commonly contain the highest Hg concentrations and are among commonly sought game fish. Presumably they pose the greatest potential risk of Hg toxicity relative to fish reproduction or consumption by other fish. In addition, we analyzed a random sampling ($n = 262$) of the remaining nonpiscivorous fish.

Stream and river sampling sites were drawn from Arizona, California, Colorado, Idaho, Montana, Nevada, North Dakota, Oregon, South Dakota, Utah, Washington, and Wyoming, on a probability basis, from the perennial stream network appearing on the 1:100, 000-scale digital line graph database of the United States Geological Survey (*22−24*). At each site, up to nine individual fish (three individuals from up to three different piscivore and nonpiscivore species) could be collected, but not all sites yielded fish.

Sample Collection and Processing for Hg Analyses. We collected fish from streams and rivers according to wadeable and nonwadeable electrofishing protocols (*25, 26*). Fish were wrapped in aluminum foil, double-bagged in resealable freezer bags, and shipped on ice to the laboratory within 36 h of being caught (*25, 26*). At the laboratory, they were inspected for condition and stored frozen at −20 °C until processing (*15*).

Freeze-Dried Sample Preparation. A second set of wet homogenate subsamples were freeze-dried for Se analysis at the same time the above samples were prepared. Since Se analysis by Instrumental Neutron Activation Analysis (INAA) requires a very small, but uniformly mixed sample, the freeze-dried samples were prepared according to a procedure prescribed by the University of Missouri Research Reactor. The full procedure is described in the Supporting Information (Methods -Se Sample Preparation).

Mercury Analysis. All Hg analyses were done on frozen wet homogenate samples by combustion atomic absorption spectrometry (CAAS) using a direct mercury analyzer (Milestone DMA80; Milestone, Monroe, CT or LECO model AMA 254; LECO Corporation, St. Joseph, MI) and EPA Method 7473 (*27*). Samples were analyzed in triplicate, and reanalyzed if the relative standard deviation (RSD) exceeded ±5%. The result for each sample was reported as the mean wet weight Hg concentration. All Hg analyses were performed within time frames that assured against nondegradation and/or changes in the Hg content of fish tissue (*28*).

Mercury Detection Limit and Quality Assurance. The analytical method detection limit (MDL) was calculated using the method of Taylor (*29*) as published in 1986 by the U.S. EPA in 40 CFR Part 136, Appendix B, Revision 1.11. The MDL was based on repeated analyses between 2000 and 2004 ($n = 875$) of a low-level standard (NIST 2976 mussel tissue) and expressed as μg Hg·g^{-1} wet wt. (assuming a water content of 70% for the mussel species used for the standard (*30*)). The MDL was calculated to be 0.015 μg Hg·g^{-1} wet wt.

We assessed analytical precision using 376 duplicate analyses of fish tissue homogenate samples within a single sample batch. Precision expressed as relative percent difference of duplicate measurements was 6.4%. We assessed systematic error of our Hg analyses by repeated analyses of two standard reference materials (SRMs) during sample analytical runs: a high-level SRM (DORM-2 dogfish tissue; Institute for National Measurement Standards (INMS), Ottawa, ON, Canada) and a low-level SRM (NIST 2976 mussel tissue; National Institute of Standards & Technology (NIST), Gaithersburg, MD). For the DORM-2 SRM (certified as 4.64 ± 0.26 μg Hg·g^{-1} dry wt.), the mean measured value was 4.58 μg Hg·g^{-1} dry wt. ($n = 1099$, SD = 0.33 μg Hg·g^{-1} dry wt., relative standard deviation [RSD] = ±7.3%), indicating a small negative bias (−1.2%). For the low-level NIST 2976 SRM (certified as 0.061 ± 0.004 μg Hg·g^{-1} dry wt.), the mean measured value was 0.070 μg Hg·g^{-1} dry wt. ($n = 876$, SD = 0.021 μg Hg·g^{-1} dry wt., RSD = ±29.8%), indicating a positive bias (14.8%) at lower concentrations.

Selenium Analysis. All Se analyses were performed on freeze-dried fish homogenate samples by standard comparator INAA according to the analysis protocol of the University of Missouri Research Reactor (*31−33*). The procedure is described briefly in Supporting Information Methods: Se Analysis.

Selenium Limit of Quantitation and Quality Assurance. The limit of quantitation (LOQ) for the INAA Se analysis of fish homogenate under this protocol is on the order of 2 ng, which on a 0.025 g sample yields a fractional mass LOQ of 0.08 μg·g^{-1} dry wt. The LOQ is based on 10 times the square root of the integrated baseline over an energy range of 160.2−163.7 keV. In gamma-ray spectroscopy, the standard deviation of the background for the measurement is the square root of the number of counts in the integrated baseline and the LOQ is 10 times one standard deviation of the background (*34*).

SRM NIST (1577 Bovine Liver; ca. 30 mg per sample) was used as an external quality control standard for the INAA measurements for two reasons. First, INAA Se analyses require small sample masses (30 mg). Thus, the 250 mg DORM-2 masses recommended by both NIST and National Research Council of Canada are incompatible with the INAA method. Second, DORM-2 and bovine liver standards behave identically relative to the INAA method. The certified value for Se in SRM 1577 is 1.1 ± 0.1 μg Se·g^{-1} dry wt. Analysis of replicate

TABLE 1. Mass and Molar Concentrations of Mercury and Selenium and Surplus Se Concentrations in Various Fish Groups[a]

fish group (n) mean total length (mm) (minimum, maximum)	mercury mean concentration (minimum, maximum)		selenium mean concentration (minimum, maximum)		surplus Se concentration (μmol Se/g wet wt) mean (std. error)
	μg Hg·g⁻¹ wet wt	μmol Hg·g⁻¹ wet wt	μg Se·g⁻¹ wet wt	μmol Se·g⁻¹ wet wt	
Non-Piscivores					
suckers (106)327 (190, 480)	0.114 (0.012, 0.468)	0.0006 (0.0001, 0.0023)	0.556 (0.112, 3.196)	0.0070 (0.0014, 0.0405)	0.0065 (0.0008)
trout and salmon (89)264 (198, 480)	0.090 (0.012, 0.662)	0.0005 (0.0001, 0.0033)	0.798 (0.080, 4.150)	0.0101 (0.0010, 0.0526)	0.0096 (0.0010)
whitefish (23)324 (235, 515)	0.088 (0.013, 0.321)	0.0004 (0.0001, 0.0016)	1.082 (0.075, 1.890)	0.0137 (0.0061, 0.1231)	0.0133 (0.0013)
carp (19)356 (180, 630)	0.067 (0.010, 0.231)	0.0003 (<0.0001, 0.0012)	1.2893 (0.453, 5.460)	0.0163 (0.0025, 0.0691)	0.0160 (0.0036])
bullheads (14)193 (165, 220)	0.115 (0.031, 0.413)	0.0006 (0.0002, 0.0021)	0.522 (0.196, 1.079)	0.0066 (0.0025, 0.0137)	0.0060 (0.0011)
other nonpiscivores (11)231 (165, 390)	0.176 (0.083, 0.285)	0.0009 (0.0004, 0.0014)	0.637 (0.274, 1.352)	0.0081 (0.0035, 0.0171)	0.0072 (0.0016)
all non-piscivores (262)296 (165, 630)	**0.103 (0.010, 0.662)**	**0.0005 (0.0000, 0.0033)**	**0.740 (0.075, 5.460)**	**0.0094 (0.0010, 0.0691)**	**0.0089 (0.0006)**
Piscivores					
pikeminnows (59)318 (142, 560)	0.368 (0.053, 1.040)	0.0018 (0.0003, 0.0052)	0.320 (0.093, 1.144)	0.0040 (0.0012, 0.0145)	0.0022 (0.0004)
walleye & sauger (50)348 (135, 570)	0.244 (0.026, 0.587)	0.0012 (0.0001, 0.0029)	0.478 (0.243, 1.102)	0.0061 (0.0031, 0.0140)	0.0048 (0.0004)
bass (48)262 (138, 485)	0.186 (0.042, 0.665)	0.0009 (0.0002, 0.0033)	0.570 (0.096, 1.869)	0.0072 (0.0012, 0.0237)	0.0063 (0.0007)
pike (30)353 (122, 640)	0.170 (0.042, 0.397)	0.0008 (0.0002, 0.0020)	0.360 (0.142, 0.638)	0.0046 (0.0024, 0.0081)	0.0037 (0.0004)
large catfish (14)401 (280, 610)	0.148 (0.049, 0.307)	0.0007 (0.0002, 0.0015)	0.657 (0.434, 1.013)	0.0083 (0.0055, 0.0128)	0.0076 (0.0006)
other piscivores (5)385 (265, 600)	0.221 (0.119, 0.3759)	0.0011 (0.0006, 0.0019)	0.607 (0.518, 0.719)	0.0077 (0.0066, 0.0091)	0.0066 (0.0007)
all piscivores (206)325 (122, 640)	**0.248 (0.026, 1.040)**	**0.0012 (0.0001, 0.0052)**	**0.452 (0.093, 1.869)**	**0.0057 (0.0012, 0.0237)**	**0.0045 (0.0002)**

[a] Surplus Selenium is the Difference in Molar Concentrations of Se and Hg.

SRM samples ($n = 61$) yielded a mean value of 1.08 μg Se·g⁻¹ dry wt. (SD = 0.063 μg Se·g⁻¹ dry wt., RSD = ±5.8%).

Effect of Measurement Precision on Se Exceedance of Hg. We explored the effect of Se and Hg measurement precision estimates, based on standard reference materials, relative to Se molar concentration of individual fish exceeding the Hg molar concentration. After conversion to wet weight molar concentrations, the precision estimates (standard deviations) of measured and certified values for the DORM-2 SRM (for Hg) and of the NIST 1577 SRM (for Se) were equal to 0.00020 μmol Hg·g⁻¹ wet wt. and 0.00022 μmol Se·g⁻¹ wet wt., respectively.

We assumed that the Se and Hg measurements were unbiased and independent, and modeled the true (but unknown) difference in molar concentration between Se and Hg as a normally distributed random variable, with mean equal to the measured difference, and standard deviation $\sqrt{(0.00020^2 + 0.00022^2)} = 0.00030$ μmol·g⁻¹ wet wt. With these assumptions, the true mean difference has a $\geq 90\%$ probability of exceeding zero (Se molar concentration > Hg molar concentration) if the measured difference exceeds 1.28 × 0.00030 = 0.00038 μmol·g⁻¹ wet wt., where 1.28 is the 90th percentile of the standard normal distribution. Thus, we considered any fish having a measured difference (Se-Hg) exceeding 0.00038 μmol·g⁻¹ wet wt. to have true Se exceeding true Hg, i.e., Se:Hg > 1. However, we did not adjust concentration statistics of Se, Hg, their difference, or their ratio for measurement precision.

Results and Discussion

Fish Samples. Selenium analyses were performed on 468 fish of 40 different species from 137 sites (some with multiple fish samples) across 12 western U.S. states (Figure 1). Fish included all of the piscivores ($n = 206$) analyzed previously for Hg by Peterson et al. (15) and a random sampling of the remaining nonpiscivores ($n = 262$) from that original sampling of 2707 large fish. As expected, the mean Hg concentration for all piscivores in Table 1 (**Bold Summary**) is greater (more than double) than the mean for all nonpiscivores. The mean Se concentration is greater for all nonpiscivores than for all piscivores. Mean Hg concentrations (μg·g⁻¹ wet wt.) by fish group in Table 1 indicate all of the piscivore groups pose a toxicity risk relative to the wildlife threshold of 0.1 μg Hg·g⁻¹ wet wt., but the nonpiscivore groups present a mixed picture. Several individual pikeminnow, walleye, sauger, bass, and pike exceed the MeHg WQC (0.3 μg·g⁻¹ wet wt. for filet) as it relates to whole fish Hg concentrations (≥ 0.185 μg·g⁻¹) (15). Based on an assessment using the MeHg WQC many individual fish in our sample likely would be recommended for limited or non-consumption by either wildlife or humans.

Selenium: Mercury Molar Ratios. Based on Se soil concentrations across our study area ranging from 0.17 to 0.74 μg·g⁻¹ dry wt (35), we expected to see many fish types and regions in the western U.S. with fish Se:Hg molar ratios <1. However, there is a general geographic pattern of Se:Hg molar ratios >1 (surplus Se), but surplus Se is not uniformly present in all fish (Figure 2 and Supporting Information Table S1).

Figure 2 suggests that Se:Hg molar ratios might decline with increasing fish size, possibly reducing Se protection in larger fish. We tested this by linear regression of surplus Se against total fish length for piscivores and nonpiscivores. The relationship for piscivores is poor ($r^2 = 0.085$) and the one for nonpiscivores is worse ($r^2 = 0.0004$). We conclude from this that Se protection against Hg toxicity in larger fish probably remains intact. The proportion of piscivores with Se:Hg <1 (11 of 206) was substancially greater than that of nonpiscivores (1 of 262 fish; $P < 0.001$, for Fisher's exact test of the difference between proportions).
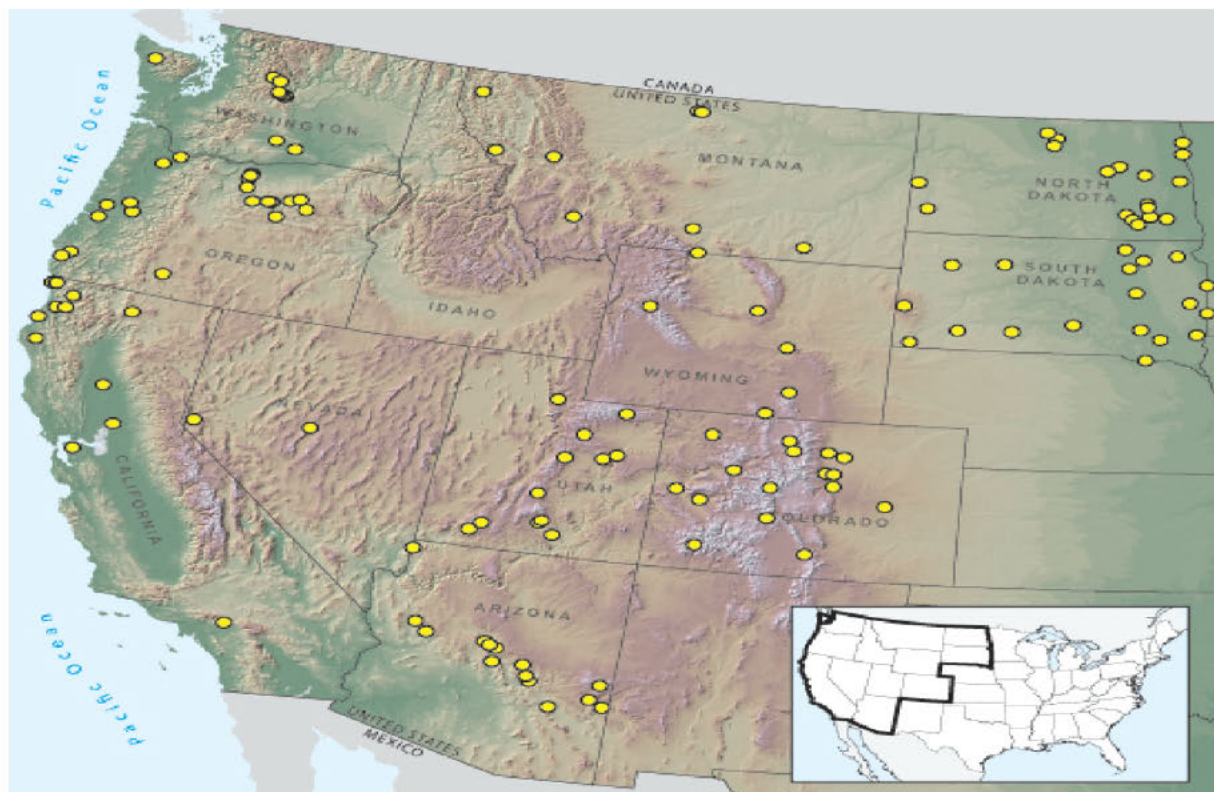
FIGURE 1. Location of probability based sites where fish tissue samples were collected for Hg and Se analysis.
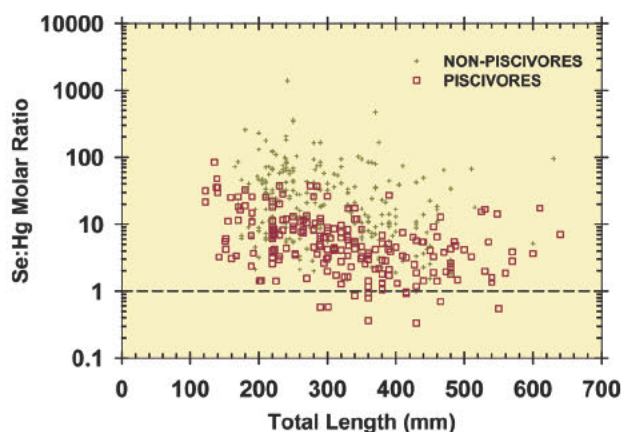
FIGURE 2. Molar ratio of selenium to mercury relative to fish size. The horizontal dotted line is the Se:Hg, 1:1 line.

Pikeminnows. All of the fish in Figure 2 that have a Se:Hg molar ratio <1 were pikeminnows (*Ptychocheilus spp.*), except the one largescale sucker (*Catostomus macrocheilus*), ranging in total length from about 300 to about 550 mm. There were 23 smaller and one larger pikeminnows with a Se:Hg molar ratio >1. This suggests that some combination of fish species, fish size and possibly environment might play a role in determining Se:Hg ratios. Northern pikeminnows represent the top of the freshwater aquatic food chain and are known to be voracious piscivores (*36*). Zimmerman (*36*) found that the stomach of pikeminnows, relative to their total weight (index of feeding (IF)) was more than twice that of smallmouth bass (*Micropterus dolomieu*). This perhaps increases Hg bioaccumulation in large pikeminnows over other piscivores due to the potential uptake from the large stomach mass. However, since pikeminnow size alone appears not to control Se:Hg molar ratios, other factors must contribute. Pikeminnows having a molar ratio of Se:Hg < 1 came from seven sites: five in Oregon, one in Montana, and one in Washington.

This suggests that local or regional environmental factors such as, wetland extent (*37*), forested regions (*38*), agricultural areas (*39*), and/or several water quality variables including pH, alkalinity, DOC, and SO_4 (*40–43*) might contribute to a molar surplus of Hg relative to Se. Zimmerman (*36*) suggested that some combination of these factors do influence the chemical burdens of fish with his finding that northern pikeminnow had significantly higher IF values in the Snake River than in the Columbia River and that stomach fullness, while significantly greater in summer than in spring in the unimpounded lower Columbia River, did not differ between seasons in the impounded reaches of the Columbia and Snake Rivers.

Mercury vs Selenium. High Hg concentrations in fish tissue from our samples were found only when Se concentrations in the same tissue were low (Figure 3). This is consistent with Belzile et al. (*44*) who found reduced bioaccumulation of Hg in all lake trophic levels (including young-of-the-year fish) downwind from the Sudbury, Ontario smelters. They concluded "Selenium plays an important role in limiting the whole-body assimilation of Hg at lower levels of the aquatic food chain." Bioaccumulation differs from, but is not entirely unrelated to, Hg toxicity potential. Concentration gradients in our study are not as well-defined geographically as those at Sudbury, but our results do suggest that fish species and environmental variability influence Se: Hg molar ratios in freshwater fish.

Mercury Criteria vs Se:Hg Molar Ratios. Peterson et al. (*15*) estimated the proportion of stream length across the western U.S. where the total Hg in fish tissue exceeded the wildlife threshold (*20*) and the current MeHg WQC (*21*). Those estimates are accurate relative to the wildlife and human health benchmarks for Hg alone, however, they likely exaggerate Hg toxicity potentials relative to an assessment based on Se:Hg molar ratios.

Considering all fish in our sample (*n*= 468), 56% exceeded the wildlife Hg threshold (0.1 μg Hg g^{-1} wet wt.) (*20*) and 12% exceeded the MeHg WQC (0.3 μg Hg g^{-1} wet wt.) (*21*). When
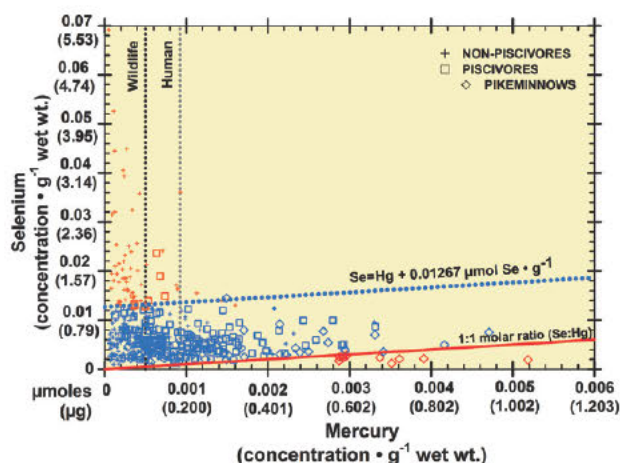
FIGURE 3. Selenium and mercury concentrations in whole fish tissue. The vertical dotted, line closest to the y-axis represents the 0.1 μg Hg·g^{-1} wet wt. whole fish wildlife threshold (20). The vertical dotted line to the right is drawn at 0.185 μg Hg·g^{-1} wet wt. whole fish (equals 0.3 μg Hg·g^{-1} wet wt. of filet), which represents the human health filet tissue based water quality criterion (21). The angled red line near the bottom of the figure is the Se:Hg, 1:1 line. The dotted blue line above and parallel to the 1:1 line is drawn at 4 μg Se·g^{-1} dry wt. = 1.0 μg Se·g^{-1} (wet wt.) = 0.01267 μmol Se·g^{-1} wet wt. above the 1:1 line and represents the surplus Se level (or toxic effect threshold (TET)) where fish exhibit reproductive failure (49). Fish shown in red below the Se:Hg, 1:1 line have a surplus of Hg. Fish shown in blue, between the red dashed 1:1 line and the blue dotted Se TET-line, presumably are protected from Hg toxicity by surplus Se. Fish shown in orange, above the blue dotted line, have surplus Se above the Se TET, and their consumers might risk Se toxic effects.

examined by major feeding groups, 33% of the nonpiscivores ($n = 262$) and 84% of the piscivores ($n = 206$), respectively, exceeded the wildlife Hg threshold. Five percent of the nonpiscivores and 25% of the piscivores exceeded the MeHg WQC. Based on Hg concentrations alone, a large proportion of the fish in our sample would exceed the MeHg WQC and possibly be unfit for consumption. However, if we consider that a molar ratio surplus of Se:Hg >1 in fish might be sufficient to prevent Hg toxicity in the fish and consumers of the fish (4), only 12 samples (those below the 1:1 line in Figure 3) would be considered unsuitable for wildlife consumption. By allowing for Se and Hg measurement uncertainty and applying that to the 1:1 line in Figure 3, only one more fish with a Hg molar surplus was added to the group. Thus, based on their Se:Hg molar ratios, 13 fish (2.7% of our total sample) might pose Hg toxicity problems for wildlife consumers. However, if we assess the potential toxicity of the 13 fish with Hg surplus (Hg >Se) based on the current MeHg WQC of 0.3 μg Hg · g^{-1} wet wt., only 6 of the 13 fish have that amount or more Hg > their 1:1 Se:Hg molar ratio. Thus, potential Hg toxicity in our entire fish sample might be no more than seven (1.3% of our sample). Since all of these fish are northern pikeminnows, this could be important to northwestern Native Americans because they commonly consume northern pikeminnows. Here we have compared the Hg surplus, relative to the Se:Hg ratio in whole fish to a human consumption criterion. We realize that such a comparison might not be directly pertinent to those human consumers of western U.S. fish who eat only the filet tissue. This discrepancy emphasizes the need to know the Se:Hg ratios in fish filet as well as in whole fish tissue.

The Se:Hg molar ratios in freshwater fish tissue have not been reported extensively. However, it has become more common for marine species. Kaneko and Ralston (45) reported Se:Hg >1 in filet of all marine fish except mako

shark. Luten et al. (19) reported similar results for marine fish filets. However, all of their freshwater fish species (pike, perch and pike-perch; $n = 21$) exhibited Se:Hg molar ratios of <1. This is in near total contrast to our results, which is not surprising, since theirs was a European study and the soils of north-central Europe and the Scandinavian countries are depauperate of Se (46). This likely contributes to the high Hg levels relative to the low Se levels observed in their freshwater fish (47). Kehrig et al. (48) measured Se and Hg in hepatic and muscle tissue of four fish species in a tropical estuary. They found the Se:Hg molar ratios were >1 (5 to 70 times >) in both tissue types of all fish. Because reports of Se:Hg ratios in freshwater fish are rare and because geographic regions differ, more documentation is needed. This is particularly true for regions of the eastern U.S. and for lakes and reservoirs that might produce Se:Hg fish tissue ratios considerably different from the ones we report here for stream fish of the western U.S.

Potential Se Toxicity. Small amounts of Se are required by all cells of virtually all forms of animal life, but Se levels above certain threshold limits can be harmful. Lemly's (49) whole body 4.0 μg Se·g^{-1} dry wt. (1.0 μg·g^{-1} wet wt., or 0.01267 μmol·g^{-1} wet wt.) toxic effect threshold (TET) is the concentration at which fish experience reproductive failure and juvenile mortality. This TET is widely cited in the literature. Thus, we used this benchmark to assess Se toxicity potential in our fish sample. There are 456 fish in Figure 3 that have a Se:Hg molar ratio >1. Presumably, all of these fish are protected against Hg toxicity. However, there are 68, or 15% of the 456 fish that have Se concentrations that exceed the Lemly (49) TET of 1.0 μg Se·g^{-1} wet wt. above the 1:1 line. This raises potential selenium toxicity (selenosis) concerns for those fish and their consumers. Thus, in our sample there are ~6 times more fish in the potential Se toxicity category than those in the potential Hg toxicity category.

Our finding that nearly all (97.5%) of the freshwater fish in our survey have sufficient Se to potentially protect them and their consumers against Hg toxicity suggests that consideration of Se−Hg interactions might improve our understanding of risks associated with fish tissue Hg toxicity. Several researchers (13, 19, 45, 50) recommend measuring Se concurrently with Hg in fish tissue and considering the Se−Hg interaction. The focus of future research should be on the Se protective mechanism itself, on the effects of co-occurring Se and Hg, and on establishing the Se:Hg molar ratios of whole fish vs filets in streams, lakes and reservoirs in various geographic settings.

Acknowledgments

Supporting Information Available

Table S1 lists all fish groups analyzed, their mercury and selenium concentrations and the selenium surpluses for each group. Additionally, details of the fish tissue sample preparation method and the selenium neutron activation analysis are described. This material is available free of charge via the Internet at http://pubs.acs.org.

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Commentary

Review of residue-based selenium toxicity thresholds for freshwater fish

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Abstract

A variety of guidelines have been proposed in recent years for linking selenium concentrations in the whole body of fish or in diet with adverse effects in fish. Diverging viewpoints seem to be forming separating groups supporting either the low selenium guidelines proposed by the government and academic researchers or the high selenium guidelines proposed by other researchers. Recently, an article was published that reviewed selected studies and recommended guidelines for selenium concentrations in the whole body of fish and in diet that were higher than those proposed by other researchers ($\approx 4 \mu g/g$ in whole body and 3 $4 \mu g/g$ in diet). That article also recommended separating guidelines for coldwater fish ($6 \mu g/g$ in whole body and $11 \mu g/g$ in diet) and warmwater fish ($9 \mu g/g$ in whole body and $10 \mu g/g$ in diet). The approaches, information, and guidelines presented in the article are reviewed and problems in their interpretation and conclusions are discussed. The majority of the selenium literature supports a whole body threshold of $4 \mu g/g$ in fish and $3 \mu g/g$ in diet.
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Keywords: Selenium; Diet; Fish; Threshold; Tissue based criteria

1. Introduction

The criteria for selenium in the aquatic ecosystem has become a controversial topic in recent years as evidenced by debate articles in the journal *Human and Ecological Risk Assessment* (Chapman, 1999; Lemly, 1999a; Hamilton, 1999; Ohlendorf, 1999; DeForest et al., 1999; Fairbrother et al., 1999), response articles (Skorupa, 1999; Fairbrother et al., 2000), and debates at national scientific meetings, i.e., "Selenium in the Environment: A Ticking Time Bomb or No Big Deal?" (SETAC, 1999). There seems to be a divergence between academia or government-backed articles proposing low-selenium criteria (SWRCBC, 1987; UCC, 1988; DuBowy, 1989; Skorupa and Ohlendorf, 1991; Pease et al., 1992; Peterson and Nebeker, 1992; Lemly, 1993a, 1996; Maier and Knight, 1994; Engberg, 1999; Skorupa, 1998; USDOI, 1998) and nongovernmental articles proposing high criteria (Canton and Van Derveer, 1997; Van Derveer and Canton, 1997; Canton, 1999;

DeForest et al., 1999; Adams et al., 2000; Brix et al., 2000).

The US Environmental Protection Agency (USEPA) is currently in the process of revising the selenium chronic criterion for the protection of aquatic life (C. Delos and K. Sappington, USEPA, written communications), which was established in 1987 (USEPA, 1987). One step in the USEPA revision process was a peer consultation workshop on the bioaccumulation and aquatic toxicology of selenium, held to discuss the technical issues underlying the freshwater aquatic life chronic criterion (USEPA, 1998). The nine-member peer review group was composed of representatives from federal agencies, academia, private consultants, and industry. The subjects of interest in the workshop included the potential development of a water-based criterion, a tissue-based criterion, and a sediment-based criterion. The general consensus of the peer review group was that the relationship between water-borne and sediment selenium concentrations to the tissue accumulation of selenium was poor because of the importance of dietary exposure in determining the potential for chronic effects. Consequently, there has been recent interest in promoting a tissue-based criterion

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or threshold (DeForest et al., 1999; Brix et al., 2000; Hamilton, 2002).

2. Critique of a tissue-based selenium threshold paper

A recent article by DeForest et al. (1999) reviewed the proposed residue-based toxicity thresholds for freshwater fish. Similar information was given in Brix et al. (2000). They proposed whole-body thresholds of 9 μg/g (all given as dry weight) for warmwater fish and 6 μg/g for larval coldwater anadromous fish, ovary threshold of 17 μg/g for warmwater fish, and fish dietary thresholds of 10 μg/g for warmwater fish and 11 μg/g for larval coldwater anadromous fish. These values are substantially different from those proposed by Maier and Knight (1994; 4.5 μg/g in tissue and 4 μg/g in diet), Lemly (1993a, 1996; 4 μg/g in whole body, 10 μg/g in ovary, and 3 μg/g in diet), and Hamilton (2002; 4 μg/g in tissue).

The DeForest et al. (1999) article seems to have fallen short of their objective of critically reviewing the proposed tissue-based thresholds for freshwater fish because they excluded the results of water-borne studies and selectively discussed results from dietary studies. Their review focused primarily on Lemly (1993a) and they correctly cite several errors in two summary tables. Those errors were corrected in Lemly (1996), which they do not cite. They also did not include information from the review article on selenium toxicology by Maier and Knight (1994) in their review. Maier and Knight (1994) independently proposed threshold concentrations for selenium effects that were similar to those of Lemly (1993a, 1996).

2.1. Errors in Lemly (1993a)

Despite the errors in Lemly (1993a), the proposed tissue-based thresholds were still supported unchanged in Lemly (1996). The residue-based thresholds proposed by DeForest et al. (1999) seem overly high and are not supported by the majority of the selenium literature. The review by DeForest et al. (1999) seems to be incomplete and does not include important articles that further supported the thresholds proposed by Lemly (1996).

Numerous authors cite Lemly (1993a) as the first comprehensive review of the selenium literature and proposal of selenium residue-based thresholds. Few authors cite Lemly (1996), which has conclusions similar to those of Lemly (1993a), but different supporting data in Tables 1 and 2, which had similar supporting citations between the two publications. No one in their publications has noted the difference in values given in Tables 1 and 2 in those two publications (Tables 1 and 2).

2.2. Additional articles supporting Lemly's proposed values

Several articles not cited in Lemly (1993a, 1996) or published later support the 4 μg/g whole-body concentration for toxic effects in fish (Hilton and Hodson, 1983; Cleveland et al., 1993; Lemly, 1993b; Hamilton et al., 1996,2001a, b) (Table 3). This effect concentration in the whole body was supported by Skorupa et al. (1996), who proposed 4–6 μg/g, and Maier and Knight (1994) who proposed 4.5 μg/g.

Likewise, several articles not cited in Lemly (1993a, 1996) or published later support the 3-μg/g dietary toxicity threshold for fish (Cleveland et al., 1993; Lemly, 1993b; Hamilton et al., 1996, 2001a, b) (Table 4). These articles report effect concentrations of 4.6–6.5 μg/g, which suggests a threshold concentration at a lower concentration, i.e., conservatively <4.6 μg/g. Those articles lend further support to the 3 μg/g threshold of effects suggested by Hilton et al. (1980), Lemly (1993a, 1996) and Skorupa et al. (1996) and the 4 μg/g threshold suggested by Maier and Knight (1994).

2.3. Information not cited in Deforest et al.

DeForest et al. (1999) cited selenium contamination problems at Belews Lake, North Carolina, Hyco Reservoir, North Carolina, and Kesterson Reservoir, California, but did not cite selenium contaminant problems at Sweitzer Lake, Colorado (Barnhart, 1957; Birkner, 1978; Butler et al., 1989, 1991, 1994, 1996) or Martin Lake, Texas (Sorensen, 1991).

Similarly, DeForest et al. (1999) cited Van Derveer and Canton (1997) as demonstrating that fish in lotic systems in Colorado were not at risk at water selenium concentrations of approximately 30 μg/L. However, they failed to mention that the articles by Canton and Van Derveer (1997) and Van Derveer and Canton (1997) had incorrectly interpreted exposure survey reports as being exposure-response studies, ignored the importance of the water-borne entry of selenium in aquatic food webs, overlooked key studies from the extensive body of selenium literature, and failed to consider the offstream consequences of proposing high instream selenium standards (Hamilton and Lemly, 1999). Offstream concerns of selenium contamination have also been discussed in Skorupa (1998) and Lemly (1999b). These offstream concerns about selenium contamination were substantiated by Radtke et al. (1988) and Radtke and Kepner (1990), who concluded that elevated selenium concentrations in sediment and biota in the backwaters of the lower Colorado River were carried by water from the upper Colorado River basin and not derived from local agricultural or industrial sources.

DeForest et al. (1999) chose to disregard the results of the SLD diet despite the more realistic exposure scenario

Table 1
Selenium concentrations in tissue associated with toxic effects in fish and aquatic organisms

Species[a]	Tissue	Lemly (1993a) selenium concentration (µg/g)[b]	Lemly (1996) selenium concentration (µg/g)[b]	Effect	Reference
Rainbow trout	Whole body	3	2	Blood changes	Hodson et al. (1980)
	Liver	12	51	Blood changes	Hodson et al. (1980)
	Whole body	5	5	Mortality	Hilton et al. (1980)
	Whole body	4	1	Mortality	Hunn et al. (1987)
Chinook salmon	Whole body	9.5	20	Reduced smolting	Hamilton et al. (1986)
	Whole body	3	2	Reduced growth	Hamilton et al. (1990)
	Whole body	10	5	Mortality	Hamilton et al. (1990)
Fathead minnow	Whole body	6	5	Reduced growth	Ogle and Knight (1989)
	Ovaries	15	24	Reproductive failure	Schultz and Hermanutz (1990)
	Whole body	8	16	Reproductive failure	Schultz and Hermanutz (1990)
Striped bass	Skeletal muscle	14	14	Mortality	Coughlan and Velte (1989)
	Whole body	NG[c]	2	Mortality	Saiki et al. (1992)
Bluegill	Skeletal muscle	20	20	Mortality	Finley (1985)
	Liver	32	34	Mortality	Finley (1985)
	Carcass	8	24	Reproductive failure	Gillespie and Baumann (1986)
	Ovaries	12	23	Reproductive failure	Gillespie and Baumann (1986)
	Whole body	5	5	Mortality	USFWS (1990)
	Whole body	16	19	Reproductive failure	Coyle et al. (1993)
	Ovaries	30	34	Reproductive failure	Coyle et al. (1993)
	Eggs	40	42	Reproductive failure	Coyle et al. (1993)
	Ovaries	10	18	Reproductive failure	Hermanutz et al. (1992)
	Skeletal muscle	10	16	Reproductive failure	Hermanutz et al. (1992)
	Liver	22	29	Reproductive failure	Hermanutz et al. (1992)
	Whole body	12	18	Reproductive failure	Hermanutz et al. (1992)
	Whole body	15	15	Teratogenic defects	Lemly (1993c)
Green alga	Whole organism	20	20	Reduced cell replication	Foe and Knight (1986)
Cyanobacterium	Whole organism	700	394	Reduced chlorophyll a	Kiffney and Knight (1990)
Cladoceran	Whole organism	20	15	Reduced weight	Ingersoll et al. (1990)
	Whole organism	30	32	Reproductive failure	Ingersoll et al. (1990)
Aquatic birds	Liver	10	NG	Reproductive failure	Skorupa et al. (in press)
	Eggs	3	NG	Reproductive failure	Skorupa et al. (in press)

[a] Rainbow trout (*Oncorhynchus mykiss*), Chinook salmon (*Oncorhynchus tshawytscha*), fathead minnow (*Pimephales promelas*), striped bass (*Morone saxatilis*), bluegill (*Lepomis macrochirus*), green alga (*Selenastrum capricornutum*), cyanobacterium (*Anabaena flosaquae*), cladoceran (*Daphnia magna*).

[b] Selenium concentrations on a dry weight basis.

[c] Not given in Lemly (1993a).

compared to the selenomethionine- (SEM) based diet in the studies with chinook salmon (*Oncorhynchus tshawytscha*) (Hamilton et al., 1990). Although there were differences in the diet formulation between the SLD-based diet and the SEM-based diet, reduced survival occurred in both dietary selenium exposures at 9.6 µg/g, and the whole-body selenium residues were remarkably similar (6.5 µg/g in the SLD diet and 5.4 µg/g in the SEM diet). Other adverse effects from the two diets were also similar between the two diets. The slight reduction in growth that occurred earlier and at slightly lower dietary concentrations in the SLD diets compared to the SEM diets was a minor discussion point in Hamilton et al. (1990).

DeForest et al. (1999) cited Brown (1997) to imply that pesticide residues in western mosquitofish (*Gambusia affinis*) used in the San Luis Drain (SLD) diet tested in Hamilton et al. (1990) may have influenced the results of dietary exposures with chinook salmon. The possibility of confounding effects from pesticides or other

Table 2
Concentrations of selenium known to be toxic in the diets of fish and wildlife

Species	Lemly (1993a) dietary selenium concentration (μg/g)[a]	Lemly (1996) dietary selenium concentration (μg/g)[a]	Effect	Reference
Rainbow trout	9	9	Mortality	Goettl and Davies (1978)
	>3	13	Mortality	Hilton et al. (1980)
	10	11	Kidney damage	Hilton and Hodson (1983)
Chinook salmon	6.5	6.5	Mortality	Hamilton et al. (1989)
	5	5	Reduced growth	Hamilton et al. (1990)
Fathead minnow	20	20	Reduced growth	Ogle and Knight (1989)
Striped bass	35	39	Mortality	Coughlan and Velte (1989)
Bluegill	50	54	Mortality	Finley (1985)
	6.5	6.5	Mortality	USFWS (1990)
	NG[b]	5	Mortality	Lemly (1993b)
	13	13	Reproductive failure	Woock et al. (1987)
	16	33[c]	Reproductive failure	Coyle et al. (1993)
Mallard duck[d]	>4	11	Reproductive failure	Heinz et al. (1987)
	>4	9	Reproductive failure	Heinz et al. (1989)

[a] Selenium concentrations on a dry weight basis.
[b] Not given in Lemly (1993a).
[c] Exposure included 10 μg/L in water.
[d] Mallard duck (*Anas platyrhynchos*).

Table 3
Selenium concentrations in tissue associated with toxic effects in fish

Exposure route, species	Tissue	Selenium concentration (μg/g)	Effect	Reference
Diet				
Rainbow trout	Carcass	4.0–4.5	Kidney damage and reduced weight	Hilton and Hodson (1983)
Fathead minnow	Whole body	43–61	Reduced growth	Bennett et al. (1986)
Bluegill	Whole body	25	Mortality	Bryson et al. (1984)
	Whole body	4.3[a]	Mortality	Cleveland et al. (1993)
	Whole body	7.9	Mortality	Lemly (1993b)
Channel catfish	Muscle	3.5	Reduced growth	Gatlin and Wilson (1984)
Razorback sucker	Whole body	3.6–8.7	Mortality	Hamilton et al. (1996)
	Whole body	5.4	Mortality	Hamilton et al. (2001a)
	Whole body	6.1	Mortality	Hamilton et al. (2001b)
Water				
Bluegill	Whole body	5.1[b]	Mortality	Cleveland et al. (1993)
Razorback sucker	Whole body	5.9	Reduced growth	Hamilton et al. (2000)
Bonytail	Whole body	9.4	Reduced growth	Hamilton et al. (2000)

[a] Derived from Fig. 3 in Cleveland et al. (1993).
[b] Derived from Fig. 2 in Cleveland et al. (1993).

contaminants in Kesterson studies has been explored, but none have been reported (i.e., Moore et al., 1990; Ohlendorf et al., 1993). Nevertheless, the toxicity of water from the SLD to fish has been reported and linked to high concentrations of major ions present in atypical ratios, to high concentrations of sulfates, or to both (Saiki et al., 1992).

In fact, in several other selenium contaminant studies, concerns about the influence of other interacting chemicals have been expressed, but none confirmed. For example, Sorensen (1986) stated that "Fish kills [at Belews Lake, NC, and Martin Lake, TX] were considered a direct result of selenium release into the main basin of the lakes because several hundred

Table 4
Selenium concentrations known to be toxic in the diets of fish

Species	Dietary selenium concentration (μg/g)	Effect	Reference
Fathead minnow	55 70[a]	Reduced growth	Bennett et al. (1986)
Bluegill	45[b]	Mortality	Bryson et al. (1984)
	6.5[c]	Mortality	Cleveland et al. (1993)
	5.1[d]	Mortality	Lemly (1993b)
Razorback sucker	2.4 5.1[e]	Mortality	Hamilton et al. (1996)
	4.6[f]	Mortality	Hamilton et al. (2001a)
	4.6[f]	Mortality	Hamilton et al. (2001b)

[a] Rotifers fed selenium laden algae.
[b] Burrowing mayfly nymphs (*Hexagenia limbata*) collected from Belews Lake, North Carolina.
[c] Selenomethionine incorporated into an Oregon moist pellet diet.
[d] Exposure included water borne exposure to 4.8 μg/L selenium and winter stress (4c).
[e] Zooplankton collected from Sheppard Bottom ponds 1, 3, and 4 at Ouray NWR, Utah.
[f] Zooplankton collected from three sites near Grand Junction, Colorado.

analyses for metals, metalloids, physiochemical parameters, and pesticides provided essentially negative results except for sufficiently high levels of selenium in the water (about 5 μg/L) to warrant concern." Others have reached similar conclusions concerning fishery problems at Belews Lake (Lemly, 1985), water and biota collected from Kesterson Reservoir area, California (Saiki and Lowe, 1987), trace elements in fish from the Merced River, and from Salt Slough, San Joaquin Valley, California (Nakamoto and Hassler, 1992), studies of Hyco Reservoir, North Carolina (Bryson et al., 1984; Gillespie and Baumann, 1986), and phosphate-mining activities in the Blackfoot River watershed of southeastern Idaho (Watson, 1998).

2.4. Water-borne versus dietary exposure

DeForest et al. (1999) did not include results from water-borne studies, but rather limited their analyses to dietary studies. In doing so, they eliminated several studies that relate directly to the tissue threshold of 4 μg/g suggested by Lemly (1993a, 1996), 4.5 μg/g of Maier and Knight (1994), and 4 μg/g of Hamilton (2002). For example, they discard the results of Hunn et al. (1987), who reported adverse effects in rainbow trout (*Oncorhynchus mykiss*), with 5.2 μg/g (assuming 75% moisture) in the whole body because it was a water-borne exposure.

Critically reviewing a residue-based toxicity threshold should include consideration of the results of water-borne studies. A selenium residue in a fish is the result of all exposures, dietary, water-borne, and sedimentary. The exposure routes are concurrent and inseparable. For example, four studies with young fall chinook salmon used different test waters and exposure routes, but had remarkably similar results based on whole-body

selenium residues (Hamilton et al., 1986, 1990; Hamilton and Wiedmeyer, 1990). In separate dietary studies, fish were exposed to either SEM in a commercially prepared diet or to the same diet made with fish meal containing elevated concentrations of naturally incorporated seleno-compounds, and reduced growth occurred in fish with whole-body residues of 4.0–5.4 μg/g (Hamilton et al., 1990). In separate water-borne studies, fall chinook salmon were exposed to water-borne selenium in two different water qualities and adverse effects (reduced growth and survival) occurred in fish with whole-body residues of 3.8–4.9 μg/g (Hamilton et al., 1986; Hamilton and Wiedmeyer, 1990). Even though the routes of exposure were different in these studies, a common whole-body selenium residue of 4–5 μg/g was associated with the same adverse effects.

The convergence of adverse effects from water-borne and dietary exposures with a variety of fish suggests that once tissue selenium concentrations reach a critical threshold, regardless of the route of exposure, adverse effects will occur. This supposition is supported by results from several studies, including Hodson et al. (1980), where rainbow trout were exposed to 53 μg/L of selenium for 308 days, but no effects were observed on the survival, growth, condition factor, or several blood and plasma measurements because whole-body selenium residues were only 1.8 μg/g. Hamilton and Wiedmeyer (1990) found no effects on mortality or growth of 2-g fall chinook salmon exposed to water-borne selenium concentrations as high as 140 μg/L for 60 days in a blended brackish water (∼1‰ salinity) because whole-body selenium residues were only 1.3 μg/g. Bertram and Brooks (1986) reported no effects on fathead minnow (*Pimephales promelas*) exposed to 7.3 μg/g in the diet and 43.5 μg/L in water for 56 days because whole-body

residues were only 2.2 μg/g. These water-borne and combined diet and water-borne exposure studies help define the upper end of the no-effect tissue threshold (1.3–2.2 μg/g) and the lower end of the effect tissue threshold (3.8–4.0 μg/g). Consequently, a threshold tissue concentration of 4 μg/g would seem reasonable.

DeForest et al. (1999) discussed their supposition that water-borne exposures result in mortality at lower whole-body selenium concentration than dietary exposures, and used Cleveland et al. (1993) as their focal point. The authors did not mention that the water-borne study was conducted with 5-month-old fish and the dietary study with 3-month-old fish, which may have influenced the data interpretation. More importantly, the selenium residue at day 60 linked to reduced mortality in the water-borne study was 4.3 μg/g and in the diet study was 5.1 μg/g. These values are very close to each other, especially considering no standard deviation or standard error was given in Cleveland et al. (1993) for readers to judge the variation of the values. If toxicity were observed at 4.3 and 5.1 μg/g, then some concentration less than these would approach the toxic effects threshold. Consequently, the data in Cleveland et al. (1993) would also support a proposed threshold of 4 μg/g. URS (2000) used a USEPA procedure (Stephan et al., 1985) with data from Cleveland et al. (1993) to calculate a whole-body toxicity threshold for selenium of 3.4 μg/g for the dietary study and 3.3 μg/g for the water-borne study. Thus, they revealed, contrary to DeForest et al. (1999), that there was no difference between water-borne and dietary exposure of bluegill (*Lepomis macrochirus*).

2.5. Coldwater fish versus warmwater fish

Another flaw in the supposition of DeForest et al. (1999) that coldwater fish are more sensitive to selenium toxicity than warmwater fish is that they reviewed selected literature and not a more complete set of selenium publications. The result is that they recommend 6 μg/g as the whole-residue threshold for coldwater fish and 9 μg/g as the threshold for warmwater fish. Several studies in Tables 1 and 3 reveal that whole-body selenium residues of 4–6 μg/g cause adverse effects regardless of whether fish were coldwater or warmwater and regardless of the route of exposure (Hilton et al., 1980; Hilton and Hodson, 1983; Hunn et al., 1987; Hamilton et al., 1990, 1996, 2001a, b; USFWS, 1990; Cleveland et al., 1993; Lemly, 1993a, b, c). DeForest et al. (1999) have not provided an adequate foundation for differentiating the importance of whole-body selenium residues between coldwater fish and warmwater fish. If 4–6 μg/g causes adverse effects in fish, then some concentration lower should be selected as the threshold concentration, i.e., 4 μg/g, not 6 or 9 μg/g as proposed by DeForest et al. (1999).

Two other publications mention the possible differences between coldwater fish and warmwater fish (USDOI, 1998; URS, 2000). Table 32 in USDOI (1998), citing Lemly (1996), gives the no-effect selenium concentration for whole-body residues as <3 μg/g in warmwater fish and <2 μg/g in coldwater fish; the level of concern as 3–4 μg/g and 2–4 μg/g, respectively; and toxicity threshold as >4 μg/g for warmwater and coldwater fish. Although Lemly (1996) does not differentiate between warmwater and coldwater fish, USDOI (1998) cited Lemly (1996) and reported a slight difference in guideline values between warmwater and coldwater fish. Even so, the values in USDOI (1998) were less than those of DeForest et al. (1999), but similar to those reported by others (Maier and Knight, 1994; Hamilton, 2002). USDOI (1998) did not discuss the basis for suggesting a difference between warmwater and coldwater fish in their sensitivity to selenium toxicity.

URS (2000) also suggests the selenium literature has some evidence of coldwater fish being more sensitive to selenium than warmwater fish. They followed the USEPA method (Stephan et al., 1985) employed by DeForest et al. (1999) to calculate the selenium tissue threshold as the geometric mean of the no observable effect concentration (NOEC) and the lowest observable effect concentration (LOEC). Application of the procedure to day 60 data for bluegill from Cleveland et al. (1993) yielded a whole-body toxicity threshold of 3.4 μg/g in their dietary study. Using day 90 data for chinook salmon from Hamilton et al. (1990), URS (2000) reported a whole-body toxicity threshold of 1.5 μg/g. Thus, they concluded there was evidence of differences in sensitivity between warmwater fish (3.4) and coldwater fish (1.5).

However, URS (2000) seems to have used inappropriate data for chinook salmon in their calculation. They note that growth of chinook salmon was reduced at 30 and 60 days of exposure to the 3.2 μg/g SLD diet and then use the whole-body selenium residue at day 90 for that treatment in the USEPA method calculation (i.e., NOEC 0.8 μg/g and LOEC 2.7 μg/g). At day 90, growth was not reduced in the 3.2-μg/g diet treatment, but was reduced in the 5.6-μg/g diet treatment. For day 60 data (NOEC 0.9 μg/g, LOEC 3.3 μg/g) the geometric mean whole-body toxicity threshold is 1.7 for chinook salmon. If day 60 data from Hamilton et al. (1990) were used in the comparison, one might still conclude there was a difference in sensitivity between coldwater fish with a threshold of 1.7 and warmwater fish with a threshold of 3.4 (Cleveland et al., 1993). However, if day 90 data were used, there would be no difference between coldwater fish with a whole-body toxicity threshold of 3.3 (NOEC 2.7 μg/g, LOEC 4.0 μg/g; Hamilton et al., 1990) and warmwater fish with a threshold of 3.9 (NOEC 3.3 μg/g, LOEC 4.6 μg/g; Cleveland et al., 1993). Considering the incongruity between day 60 and day 90

data from these two studies, there seems to be little support for differentiating sensitivity to selenium toxicity between coldwater and warmwater fish.

2.6. Diet selenium threshold

DeForest et al. (1999) proposed a dietary selenium threshold of 11 µg/g for coldwater fish and 10 µg/g for warmwater fish. The available information suggests similar sensitivity between coldwater fish and warmwater fish to dietary selenium toxicity. Tables 2 and 4 reveal that 4.6–6.5 µg/g dietary selenium causes adverse effects in fish regardless of whether they are coldwater species or warmwater species (Hamilton et al., 1989, 1990, 2001a, b; USFWS, 1990; Cleveland et al., 1993; Lemly, 1993a, b). If these dietary concentrations cause adverse effects in fish, primarily mortality, then a lower concentration must be selected as a dietary threshold concentration, i.e., 3 µg/g.

Professional judgment is an important consideration in the interpretation of data that can be frequently difficult and complex, conflicting or ambiguous, or incomplete (USEPA, 1992). Over 20 years ago, Hilton and colleagues conducted several selenium toxicity studies in the late 1970s and early 1980s and, based on their scientific judgment, they hypothesized that >3 µg/g dietary selenium would be harmful to fish over the long term (Hilton et al., 1980). Research in the late 1980s through the early 2000s has substantiated the speculation of John Hilton and colleagues.

3. Divergence of selenium thresholds

Much of the controversy in recent years concerning the selenium criterion for aquatic life and the dichotomy in proposed toxicity thresholds has been between government/academia published papers and nongovernmental papers. It is incumbent on federal government scientists to be an advocate for the environment on behalf of the general public as stated in the mission statement of the US Department of the Interior. Some may state this is a biased position. The chief biologist of the National Biological Service (NBS), and later the Biological Resources Division of the US Geological Survey, Dennis Fenn noted that the line is thin between judgment informed by sound scientific data and speculative judgment based on little data and much personal interest (Fenn and Milton, 1997); yet he concluded NBS scientists must be advocates for the environment (Fenn and Milton, 1997; Fenn, 1997). As Fenn stated, a basic premise of the scientific method is that the scientist has no vested interest in the outcome of the observations. DeForest et al. (1999) have attempted to critically evaluate selenium thresholds for fish. Others have attempted similar critical evaluations of thresholds using

limited datasets for fish (Brix et al., 2000) and birds (Adams et al., 1998, 2000; Fairbrother et al., 1999). Skorupa (1999) critiqued the article by Fairbrother et al. (1999) and noted the selective use of data from several studies that resulted in higher selenium threshold values for birds than proposed by government researchers. Fairbrother et al. (2000), in turn, responded to Skorupa (1999). Skorupa (personal communication) had similar comments on the draft of Adams et al. (1998). Articles that use limited datasets do little to enhance the body of knowledge about selenium. In contrast, to meet our responsibilities as federal researchers for stewardship of our natural resources for the benefit of our citizens, it is incumbent on us to ensure that the full range of relevant information is acquired and presented to the public. This responsibility requires us to not only point out deficiencies of selective information presented in scientific papers such as DeForest et al. (1999) and Brix et al. (2000), yet work to complement their data with the widest possible range of data.

Arguments in the articles by DeForest et al. (1999), Brix et al. (2000), Fairbrother et al. (1999), and Adams et al. (1998) for high threshold values were supported by statistics. However, Skorupa (1999) pointed out how selective use of data points can lead to the arrival at erroneous conclusions. Many of the concerns raised in this critique of DeForest et al. (1999) match those expressed by Stoto (1990) who noted that errors in conclusions could result from incomplete and inaccurate reporting of data, i.e., incomplete and inaccurate review of the selenium literature.

4. Conclusions

DeForest et al. (1999) and Brix et al. (2000) have used selective data to present high toxicity threshold for selenium in the tissue and diet of fish. They have cited older literature containing errors (Lemly, 1993a) while omitting later literature with corrected values (Lemly, 1996), excluded data from publications based on minor justifications, and overlooked key studies from the extensive body of selenium literature. The proposed high-selenium thresholds by DeForest et al. (1999) and Brix et al. (2000) does not stand on equal footing with reviews of more extensive datasets by USDOI (1998), Lemly (1996), Maier and Knight (1994), and Hamilton (2002). Recent studies continue to support the dietary selenium threshold of 3 µg/g and the whole-body selenium threshold of 4 µg/g for fish.

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Palmer Hough/DC/USEPA/US

01/04/2011 04:54 PM

To   Christopher Hunter

cc   Brian Topping

bcc

Subject   Fw: Spruce Mitigation Comment Response

Chris:

Here are the revised mitigation RTC for the RD. Kudos to Greg Pond and Brian T.

-Palmer

ATTACHMENT REDACTED – DELIBERATIVE

2010-01-02 Mitigation Comments-Responses of Potential Concern_GP-BT-PH_edits.docx

Palmer Hough, Environmental Scientist
tel: 202.566.1374 I fax: 202.566.1375

Wetlands Division
U.S. EPA Headquarters (MC 4502T)
1200 Pennsylvania Avenue, NW
Washington, DC 20460
www.epa.gov/wetlands

----- Forwarded by Palmer Hough/DC/USEPA/US on 01/04/2011 04:53 PM -----

From:	Brian Topping/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA
Date:	01/04/2011 08:08 AM
Subject:	Fw: Spruce Mitigation Comment Response

Palmer
Attached are my edits on top of Greg's and incorporating the thoughts below.
I don't believe the comments that this question is new and so cross referenced answers are insufficient.
These are not new arguments - mostly restated repetition.
Let me know if you want to discuss,
Brian
[attachment "2010-01-02 Mitigation Comments-Responses of Potential Concern_GP-BTedits.docx"
deleted by Palmer Hough/DC/USEPA/US]

Brian Topping
US Environmental Protection Agency
Wetlands Division, Room 7231
Office: 202-566-5680, FAX: 202-566-1375
Mail Code 4502T, 1200 Pennsylvania Avenue, NW, Washington, DC 20460
Deliveries: EPA West -- Room 7231-S, 1301 Constitution Avenue, NW, Washington, DC 20004
topping.brian@epa.gov
----- Forwarded by Brian Topping/DC/USEPA/US on 01/04/2011 08:03 AM -----

From: Greg Pond/R3/USEPA/US

Here is quick response from Brent Johnson on Fritz et al criticisms of the 2010 NABS paper. This needs to be inserted somehow into 278A

(b) (5)

Greg Pond
Office of Monitoring and Assessment
U.S. EPA Region 3
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
(p) 304-234-0243
(f) 304-234-0260
pond.greg@epa.gov
Website: http://epa.gov/reg3esd1/3ea50.htm

Greg Pond	FYI--I sent Ken Fritz and Brent Johnson a clip fr...	01/03/2011 02:58:24 PM

From:	Greg Pond/R3/USEPA/US
To:	Brian Topping/DC/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA

FYI--I sent Ken Fritz and Brent Johnson a clip from TED critique of their paper. Will send along any responses they might make.

Greg Pond
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U.S. EPA Region 3
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
(p) 304-234-0243
(f) 304-234-0260
pond.greg@epa.gov
Website: http://epa.gov/reg3esd1/3ea50.htm

| Brian Topping | Greg, Please send your revisions to Chris, Palm... | 01/03/2011 01:55:31 PM |

From:	Brian Topping/DC/USEPA/US
To:	Greg Pond/R3/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, Palmer Hough/DC/USEPA/US@EPA
Date:	01/03/2011 01:55 PM
Subject:	Spruce Mitigation Comment Response

Greg,

Please send your revisions to Chris, Palmer and I when you finish up today so we can review / build from there.

Thanks,

Brian

_____

Brian Topping
US Environmental Protection Agency
Wetlands Division, Room 7231
Office: 202-566-5680, FAX: 202-566-1375
Mail Code 4502T, 1200 Pennsylvania Avenue, NW, Washington, DC 20460
Deliveries: EPA West -- Room 7231-S, 1301 Constitution Avenue, NW, Washington, DC 20004
topping.brian@epa.gov

I'll get you some in about 15 minutes (68-113). Definitely don't want you to be bored at all over the next several days.

mk

\---

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

	Kevin Minoli	I'm through the first 10 of these and will get throu...	01/04/2011 05:24:56 PM

From:	Kevin Minoli/DC/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Date:	01/04/2011 05:24 PM
Subject:	Re: RD responses 1A-67A for your review

I'm through the first 10 of these and will get through another 10-20 before I leave, so if you have another slug that you could send by 6:15 that would be super. Thanks.

	Matthew Klasen	Hi Kevin, Here's the next batch for you: WVDEP...	01/04/2011 03:07:45 PM

From:	Matthew Klasen/DC/USEPA/US
To:	Kevin Minoli/DC/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/04/2011 03:07 PM
Subject:	Re: RD responses 1A-67A for your review

Hi Kevin,

Here's the next batch for you: WVDEP comments 1B-38B. Chris flagged one legal sentence (highlighted) in the response to 2B that may no longer be in the FD. This may be worth just deleting.

Other than that, all of these responses should be ready for your review. We'll work to get you another subset of these to look at hopefully by COB today, which should be 68A-110A or so. Let us know your progress this afternoon on these.

Thanks,
Matt

[attachment "2011-01-04 Compiled WVDEP RD Comment Responses.doc" deleted by Kevin Minoli/DC/USEPA/US]

\---
Matt Klasen
U.S. Environmental Protection Agency

Office of Water (IO)
202-566-0780
cell (202) 380-7229

	Kevin Minoli	Matt- Attached are my comments on the first bat...	01/04/2011 02:37:33 PM

From: Kevin Minoli/DC/USEPA/US
To: Matthew Klasen/DC/USEPA/US@EPA
Cc: Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date: 01/04/2011 02:37 PM
Subject: Re: RD responses 1A-67A for your review

Matt- Attached are my comments on the first batch. Obviously a tremendous amount of work has gone into crafting these responses and for the most part my suggestions are pretty easy to incorporate. (b)(5) Attorney Client Privilege

Thanks, Kevin

[attachment "2011-01-03 RD 1A-67A for Kevin's review.ksm.docx" deleted by Matthew Klasen/DC/USEPA/US]

	Matthew Klasen	Hi Kevin, Here are RD comment responses #1A-...	01/03/2011 06:04:50 PM

Hi Kevin,

Here are RD comment responses #1A-67A for you to begin your long RD comment review. Huge thanks to everyone who helped pull these together.

A few notes:

- The header explains the highlighting scheme, but to reiterate here: Yellow highlighted comments mean comments are new; non-highlighted comments can be answered with just a PD cross-reference. We'll remove the highlighting before we finalize the document.

- There are three responses not yet ready for your review, which we've **highlighted in teal**:
    - **14A** (materials handling);
    - **30A** (outfall 015 and underground mining); and
    - **67A** (selenium assumptions).
  The remaining 64 responses should be good to go.

- We know that some of these comments/responses will require changes to the FD, and Chris will be working to make those changes concurrently with your review.

Let us know tomorrow how your review is progressing so that we can be ready with the next chunk.

And for context, there are four main chunks of RD comments: **1A-67A** (this batch), **68A-242A** (mostly conductivity issues), **243A-307A** (mitigation), and **1B-39B** (WVDEP comments).

Let me know if you have any questions.

Thanks,
Matt

[attachment "2011-01-03 RD 1A-67A for Kevin's review.docx" deleted by Kevin Minoli/DC/USEPA/US]

Julia McCarthy/R8/USEPA/US

01/04/2011 06:48 PM

To   Christopher Hunter

cc

bcc

Subject   Spruce Executive Summary

Chris,
Hope this works better... Let me know if you want me to add/change anything.
Cheers,
Julia

ATTACHMENT REDACTED – DELIBERATIVE

Spruce ES_010411.doc
Julia McCarthy
on detail to USEPA Headquarters
Office of Wetlands, Oceans and Watersheds
(202) 566-1660
mccarthy.julia@epa.gov

A land ethic, then, reflects the existence of an ecological conscience, and this in turn reflects a connection of individual responsibility for the health of the land. Health is the capacity of the land for self-renewal. Conservation is our effort to understand and preserve this capacity. ~Aldo Leopold

Kevin Minoli/DC/USEPA/US	To	Matthew Klasen	
01/04/2011 10:55 PM	cc	Gregory Peck, Karyn Wendelowski, Margaret Passmore, Stefania Shamet	
	bcc		
	Subject	Responses to 68A-113A	

.

Thanks, Kevin

ATTACHMENT REDACTED – DELIBERATIVE

2011-01-04 68A-113A for Kevin.ksm.docx
Your next batch

Your next batch

Matthew Klasen   to: Kevin Minoli   01/04/2011 05:56 PM

Cc: Stefania Shamet, Margaret Passmore, Gregory Peck, Karyn Wendelowski

---

Hey Kevin,

So here's your next batch: 68A-113A. This picks up where you left off on 1A-67A yesterday.

Based on talking with Chris, we'll probably get you the mitigation section (243-307) as the next batch tomorrow morning. Let me know if you have any questions on these. We'll work to get the mitigation section ready and will start incorporating your comments on 1-67A from earlier today.

Thanks,
Matt

[attachment "2011-01-04 68A-113A for Kevin.docx" deleted by Kevin Minoli/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Matthew Klasen/DC/USEPA/US

01/04/2011 10:57 PM

To   Christopher Hunter

cc

bcc

Subject   Fw: Responses to 68A-113A

Here are Kevin's comments on the most recent batch; obviously he's lapping us in terms of getting these back.

I'll take a look at the mitigation section tonight / tomorrow AM, in prep for getting him something pretty early tomorrow.

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

-----Forwarded by Matthew Klasen/DC/USEPA/US on 01/04/2011 10:56PM -----

To: Matthew Klasen/DC/USEPA/US@EPA
From: Kevin Minoli/DC/USEPA/US
Date: 01/04/2011 10:55PM
Cc: Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Subject: Responses to 68A-113A

(b) (5)

Thanks, Kevin

(See attached file: 2011-01-04 68A-113A for Kevin.ksm.docx)
Your next batch

Your next batch

M	to Kevin Minoli	01/0
att	:	4/20
he		11
w		05:5
Kl		6
as		PM
en		

Hey Kevin,

So here's your next batch: 68A-113A. This picks up where you left off on 1A-67A yesterday.

Based on talking with Chris, we'll probably get you the mitigation section (243-307) as the next batch tomorrow morning. Let me know if you have any questions on these. We'll work to get the mitigation section ready and will start incorporating your comments on 1-67A from earlier today.

Thanks,
Matt

[attachment "2011-01-04 68A-113A for Kevin.docx" deleted by Kevin Minoli/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780

cell (202) 380-7229 [ ] - 2011-01-04 68A-113A for Kevin.ksm.docx

ATTACHMENT REDACTED – DELIBERATIVE

Stefania Shamet/R3/USEPA/US

01/05/2011 07:03 AM

To Matthew Klasen

cc Christopher Hunter

bcc

Subject 114A-140A

(b) (5)

Plan for the day:

Skipping the 930 check in.

(b) (5)

1pm Sussman briefing

Other than that, I'm going to keep going through these.

(b) (5)

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responsessds.docx

Matthew
Klasen/DC/USEPA/US
01/05/2011 08:58 AM

To   Christopher Hunter
cc
bcc
Subject   Re: Feedback on press release

OK, will do.

By the way, here's what I pulled together yesterday (which I'll merge with yours).

mk

          ATTACHMENT REDACTED - DELIBERATIVE

2010-01-04 Outline for Pete Briefing.docx

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

| Christopher Hunter | I'm going to be in a lot of meetings today, so I th... | 01/05/2011 08:45:07 AM |

From: Christopher Hunter/DC/USEPA/US
To: Matthew Klasen/DC/USEPA/US@EPA
Date: 01/05/2011 08:45 AM
Subject: Re: Feedback on press release

I'm going to be in a lot of meetings today, so I thought I would get this done early. We'll see if Tanya has
any response, but feel free to combine this doc with yours.

Chris
[attachment "Comments and Responses for Denise.docx" deleted by Matthew Klasen/DC/USEPA/US]

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

| Matthew Klasen | Ok -- I put together a really basic outline to talk fr... | 01/05/2011 08:37:06 AM |

From: Matthew Klasen/DC/USEPA/US
To: Christopher Hunter/DC/USEPA/US@EPA
Date: 01/05/2011 08:37 AM
Subject: Re: Feedback on press release

Ok -- I put together a really basic outline to talk from yesterday on the comments; I'll send that to you
shortly if that helps.

(b) (5)

Matt Klasen
U.S. Environmental Protection Agency
Office of Water
(202) 566-0780
Cell (202) 380-7229

   Christopher Hunter

   ----- Original Message -----
      From: Christopher Hunter
      Sent: 01/05/2011 08:31 AM EST
      To: Matthew Klasen
      Subject: Re: Feedback on press release
Thanks Matt.

Also, we've got the meeting this afternoon with Denise on the comments and responses, and I'm trying to put together a 1 pager of bullets to help frame the discussion. (b) (5) ████████████████████████████████ ██ See what you think and edit as you like,

Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Matthew Klasen	I'll pick it up when I get in (about 20 min -- later t...	01/05/2011 08:28:38 AM

From:	Matthew Klasen/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Date:	01/05/2011 08:28 AM
Subject:	Re: Feedback on press release

I'll pick it up when I get in (about 20 min -- later than usual -- must be lack of sleep).

I'll scan them and send to you, Dave, and Denise, and leave the hard copy with Greg to make changes and re-send to OEA.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water
(202) 566-0780
Cell (202) 380-7229

   Christopher Hunter

   ----- Original Message -----
      From: Christopher Hunter
      Sent: 01/05/2011 08:15 AM EST

To: Nancy Stoner
Cc: David Evans; "Denise Keehner" <keehner.denise@epa.gov>; Matthew Klasen
Subject: Re: Feedback on press release

Thanks Nancy,

Matt or I will be by later today to pick up the edits. Also, we should have a revised draft of the executive summary for your review later today or tomorrow morning.

Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Nancy Stoner	My proposed line edits will be on Martha's desk...	01/05/2011 07:44:53 AM

From:	Nancy Stoner/DC/USEPA/US
To:	"Denise Keehner" <keehner.denise@epa.gov>, David Evans/DC/USEPA/US@EPA, "Christopher Hunter" <Hunter.Christopher@epamail.epa.gov>
Date:	01/05/2011 07:44 AM
Subject:	Feedback on press release

My proposed line edits will be on Martha's desk when I get in (by 9). Not difficult. Thx

Christopher Hunter/DC/USEPA/US	To	Julia McCarthy
01/05/2011 09:15 AM	cc	
	bcc	
	Subject	Re: Spruce Executive Summary

Thanks

ATTACHMENT REDACTED – DELIBERATIVE

Spruce ES - ch.doc

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Julia McCarthy	Chris, Hope this works better... Let me know if y...	01/04/2011 06:48:58 PM

From:	Julia McCarthy/R8/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Date:	01/04/2011 06:48 PM
Subject:	Spruce Executive Summary

Chris,
Hope this works better... Let me know if you want me to add/change anything.
Cheers,
Julia
[attachment "Spruce ES_010411.doc" deleted by Christopher Hunter/DC/USEPA/US]
Julia McCarthy
on detail to USEPA Headquarters
Office of Wetlands, Oceans and Watersheds
(202) 566-1660
mccarthy.julia@epa.gov

A land ethic, then, reflects the existence of an ecological conscience, and this in turn reflects a connection of individual responsibility for the health of the land. Health is the capacity of the land for self-renewal. Conservation is our effort to understand and preserve this capacity. ~Aldo Leopold

Matthew Klasen/DC/USEPA/US

01/05/2011 09:16 AM

To Gregory Peck

cc Brian Frazer, Christopher Hunter, Karyn Wendelowski, Kevin Minoli, Stefania Shamet

bcc

Subject Re: 9:30 meeting

Unfortunately Chris and Stef won't be joining us at 9:30 so our Se expertise will be more limited -- but let's chat. Also should discuss the "prohibit and withdraw" issue.

Kevin: I'm working through the mitigation section now and should have you that section a bit later this morning.

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Gregory Peck	I'll open the line at 9:30 for folks that are availabl...	01/05/2011 09:13:47 AM

From:	Gregory Peck/DC/USEPA/US
To:	Karyn Wendelowski/DC/USEPA/US@EPA
Cc:	Brian Frazer/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/05/2011 09:13 AM
Subject:	Re: 9:30 meeting

I'll open the line at 9:30 for folks that are available to talk.
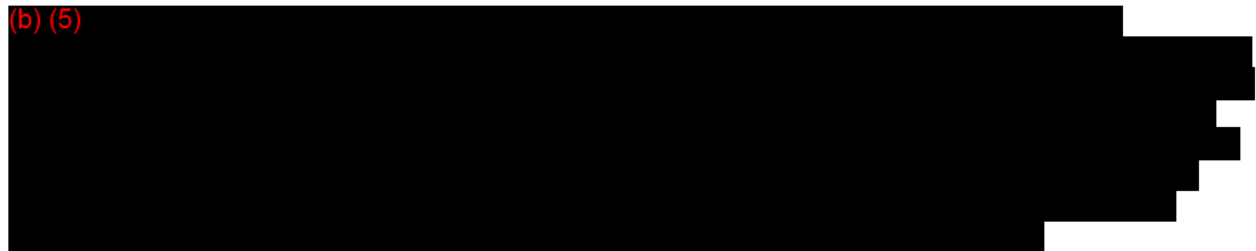
Karyn Wendelowski	(b) (5)	01/05/2011 09:11:39 AM

From:	Karyn Wendelowski/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Cc:	Brian Frazer/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/05/2011 09:11 AM
Subject:	Re: 9:30 meeting

(b) (5)

9:30 meeting

Christopher Hunter	to:	Matthew Klasen, Karyn Wendelowski, Kevin Minoli, Gregory Peck, Brian Frazer, Stefania Shamet	01/05/11 08:10 AM

I probably won't be able to make the 9:30 meeting this morning since I'll be going over to FHWA for a meeting. I didn't have much to report except that we've drafted a new version of the executive summary per Nancy's request and incorporated her edits to the main body. I'll likely be circulating the new exec summary later today.

(b) (5)

Thanks

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

These are a couple of sample briefing papers. this is the format we need to use.

Mining_ECP_Briefing Paper_CoalMac 6-11.doc   Hobet 45_ECP_briefing_Rvs 11-23-09.doc

ATTACHMENTS REDACTED –
DELIBERATIVE

Here are a couple of end of 60-day letters. The one for Spring Branch should be a bit easier. We'll have to modify to make recommendations though.

Hobet No 45 End of 60 Day.PDF   CoalMac 60 day letter 6.21.10.PDF

Here's an example from Region 4.

final letter 121410 Leeco-Stacy Branch LRL-2007-0217 897-0480.pdf

Jessica Martinsen
U.S. EPA Region III
Office of Environmental Programs
1650 Arch St. (3EA30)
Philadelphia, PA 19103
215-814-5144 (office)
215-814-2783 (fax)

JAN – 4 2010

Colonel Robert D. Peterson
District Engineer
Huntington District
U.S. Army Corps of Engineers
502 Eighth Street
Huntington, West Virginia 25701

Re: Public Notice 200800791; Hobet Mining, LLC; Surface Mine No. 45, Lincoln County, West Virginia

Dear Colonel Peterson:

The U.S. Environmental Protection Agency (EPA) has been participating in discussions with your staff and with company representatives of Hobet Mining, LLC to seek resolution to concerns expressed by our agency for the proposed Surface Mine No. 45 project. Hobet Mining, LLC's Surface Mine No. 45 is one of the 21 projects located in West Virginia identified for the enhanced coordination process (ECP) provided in the Memorandum of Understanding (MOU) signed by our respective agencies and the Department of Interior on June 11, 2009. The 60-day ECP timeframe began on November 2, 2009 and will expire today. These discussions have resulted in an agreement which addresses our concerns. Therefore, EPA believes the Corps may finalize their permit decision without further comment by EPA under the ECP.

During the project review process as provided by the June 11, 2009 Memorandum to the Field, EPA identified four areas of general concern. These included avoidance and minimization, water quality impacts, cumulative effects, and mitigation. The original project as proposed by Hobet Mining, LLC would have impacted 32,690 linear feet of stream channel and disturbed 602 surface acres. The streams on-site are good quality and are providing clean, freshwater dilution to the Mud River, an impaired stream.

Hobet Mining, LLC has addressed our concerns through a series of proposed actions. First, they have reduced physical stream impacts by nearly 50% to 16,267 linear feet of stream channel. These avoidance and minimization measures have been incorporated in a manner that still allows for extraction of 91% of the coal reserves originally proposed to be mined. Hobet Mining, LLC has also changed the mine design to incorporate upfront measures that are expected
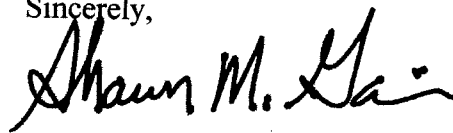
to be protective of water quality impacts. There are two receiving streams downstream of the mined area, Berry Branch and Stonecoal Branch. Based on the regional geology, there is a low expectation of any base flow discharge from the ponds in Berry Branch. In Stonecoal, the coal will be mined below the level of the stream and, therefore, any water infiltrating the backfilled area will have a low probability of discharging.

While EPA reasonably believes that in light of the regional geography and revised mining configuration water quality will be protected, to address water quality concerns should they arise, all parties have agreed to the enclosed monitoring plan and the implementation of the enclosed adaptive management plan. Finally, the applicant has agreed to biological, chemical and physical success criteria as part of the compensatory mitigation plan and is preserving 5,286 linear feet of Stonecoal Branch from future mining impacts. The implementation of mitigation success criteria will assure that the functions, including chemical and biological parameters, of the impacted waters will be replaced.

We appreciate the work your staff and Hobet Mining, LLC have undertaken to address the Agency's concerns. With the incorporation of the project modifications as described above into enforceable conditions within the Section 404 permit, EPA believes that a permit decision may move forward. In addition, we request a copy of the permit be sent to Hobet Mining, LLC for signature.

Sincerely,

Shawn M. Garvin
Regional Administrator

Enclosures

STONECOAL / BERRY BRANCH MONITORING PLAN

Chemical Monitoring Parameters

Each sample will be monitored for:
- Flow
- pH
- Iron
- Manganese
- Aluminum
- Selenium
- TDS
- TSS
- Conductivity
- Calcium
- Potassium
- Magnesium
- Sulfate
- Bicarbonate Alkalinity
- Chloride
- Sodium
- Total alkalinity
- Carbonate alkalinity

Chemical Sampling Frequency

Each agreed sampling location will be sampled two times per month. The sampling day of the month, for each sampling location, will be consistent month to month. As an example, Stonecoal #2 would always be sampled on the first Tuesday and third Tuesday of the month. To ensure comparison within a watershed the sampling in Berry Branch will be conducted on one day and in the Stonecoal watershed on another.

Chemical Sampling location

A map depicting all chemical sampling locations will be provided to the Corps and to EPA. All of the NPDES points will be included in the sampling protocol; the actual sampling point will be at the discharge from the sediment control structure.

In addition to the NPDES points there will be additional sampling points upstream of the upmost NPDES point on Stonecoal and downstream of the lowest NPDES point, just upstream of the confluence with Mud River. Similarly there will be a downstream monitoring point on Berry Branch just upstream of the confluence with Mud River. These downstream monitoring points are coincident with the Surface Water Baseline Monitoring Points used in the SMCRA permit.

In Berry Branch, the existing NPDES monitoring points on the south side of the stream, from the Hobet 44 permit, will be subject to this enhanced sampling protocol.

As a control, one of the watersheds that flow south into Stonecoal will be included in the monitoring plan.

Chemical Sampling Site

Each of the selected sampling sites will be prepared to allow repetitive reproducible sampling results. These site upgrades include the construction of concrete weirs at each NPDES point with permanent "V" notches to improve flow measurement.
For the in-stream sampling points in both Stonecoal and Berry Branch the cross section will be surveyed and permanent depth gauges installed.

Biological Monitoring

In addition to the twice monthly sampling benthic sampling will be conducted three (3) times per year: winter (Jan-Feb), spring (March-May), and summer (June-Sept), using the WVDEP standard field and laboratory methods, at the downstream monitoring points in both Stonecoal and Berry Branch and at upstream control sites, above the proposed mining disturbance. No benthic sampling will be conducted between October and January. A map depicting all biological sampling locations will be provided to EPA and the Corps. The WVDEP protocol shall be followed closely, including the use of a random 200 (±20%) organism fixed-subsample for calculation of the WVSCI. Although WVDEP currently use family-level macroinvertebrate taxonomy, genus-level identifications (excluding the family Chironomidae) shall accompany the WVSCI. In addition to WVSCI metrics, genus-level EPT richness, Ephemeroptera Richness, Plecoptera Richness, Clinger Taxa Richness, and % Ephemeroptera will be provided, at a minimum, for each sample.

Data Submittal

All of the collected monitoring data will be reported in raw (chemical values and taxa) and summarized format (e.g., WVSCI and metrics) within five (5) working days of receiving the sample results from the respective laboratories on a dedicated ftp site. Password protected access to this ftp site and the information on this site will be provided to both EPA and the CoE.

Quality Assurance

Replicate chemical samples should be collected at one site during each sampling trip. A field blank sample should be collected once per sampling trip to document that there is no contamination from containers or samplers. Preservative blanks should also be run for each trip to ensure that any preservatives are free of contaminants.

A replicate biological sample (properly labeled and preserved in ethanol) should be collected at one of the monitoring stations each season, and sent to EPA Region III-Wheeling for a quality assurance comparison check of biological field and lab methodologies. Additionally, one of the

biological samples per season should be sent to EPA Region III-Wheeling for a quality assurance check of taxonomic classification.

ADAPTIVE MANAGEMENT PLAN FOR CHANGES IN CONDUCTIVITY

Background

Recent studies conducted by the US Environmental Protection Agency have reported a correlation between the condition of benthic macroinvertebrate communities and conductivity. These findings were published in July 2008 by Greg Pond, Margaret Passmore and others in the Journal of the North American Benthological Society. The study evaluated 27 mined sites with valley fills. The proposed Hobet 45 permit does not include any valley fills.

The proposed permit does have discharges from sediment control structures that are constructed to collect and discharge surface water runoff from the mined area. There are two receiving streams downstream of the mined area, Berry Branch and Stonecoal Branch. Stonecoal Branch is down dip of the mining area and Berry Branch is up dip. Based on the regional geology, as described below, there is a low expectation of any base flow discharge from the ponds in Berry Branch.

In Stonecoal Branch, the coal will be mined below the level of the stream and therefore any water infiltrating the backfilled area will have a low probability of discharging. Based on the configuration of the mining, the water quality and quantity conditions experienced in a conventional valley fill where there is a perennial discharge at the toe of the fill are not expected to occur at this site. These issues are further discussed in Appendix B

As part of the permitting action it is proposed to conduct increased monitoring of the discharge from the sediment control structures and also the receiving streams. This increased monitoring will also include benthic sampling.

This adaptive management plan is to define an approach if elevated levels of conductivity greater than the baseline condition occur and is intended to address changes in water quality that could cause excursions from numeric or narrative water quality criteria if unaddressed.

Baseline Condition

As part of the SMCRA permit, baseline data for both Stonecoal Branch and Berry Branch were collected. The conductivity data from this sampling is detailed in the Table included as Appendix A to this document.

Actions

As there is no numeric water quality criterion for conductivity, combined with the concern that increases in conductivity may effect the condition of the benthic community and excursions from the narrative criterion associated therewith, the proposed plan is based on two components; the trends in conductivity from both the tributaries and the mouth of Stonecoal and Berry Branches plus definitive actions if there are repeated exceedances of the calculated threshold values.

Trend Analysis

The results from each of the twice-monthly enhanced chemical monitoring points will be plotted separately as a time series in order to determine if there are any trends in the conductivity levels. For the purpose of the analysis the actual value used will be the conductivity multiplied by the measured flow. This calculated value will not be used for threshold identification (see below). In addition, as the overall impact on both watersheds is the critical component of the analysis, the results from each sampling sweep (conductivity multiplied by flow) in Berry Branch and Stonecoal Branch will also be summed and the results plotted as a time series. These results will be conductivity multiplied by flow. There will be a separate plot for Berry Branch and Stonecoal Branch.

The threshold for the implementation of the adaptive management plan will be 300 μmhos in all tributaries and Stonecoal Branch, and 500 μmhos at the mouth of Berry Branch. These endpoints represent a threshold-response value that strongly correlates to biological impairment in small Central Appalachian streams.

If the linear trend of the Conductivity multiplied by Flow indicates that the result will exceed the threshold (tributaries or mouth of Berry and Stonecoal Branches) multiplied by the threshold flow within a 12-month period then the applicant will conduct a detailed analysis of the reasons for increased conductivity. A sample worksheet is attached as Appendix C. The applicant shall submit a report to the Corps and EPA describing this analysis within 30-days after three consecutive sets of sampling indicate that the trend will exceed the threshold. The report also shall include proposed actions to address the increased conductivity. The proposed actions to address the increased conductivity will be implemented within 45 days following written approval by the Corps, EPA, and any other appropriate regulatory authority.

The potential techniques that may be employed include, but are not limited to; revisions to material handling plans, revisions to the in-pit storage of stormwater; grading and vegetation of reclaimed areas, addition of pre-treatment ponds, and internal stormwater diversion.

Exceedance

The conductivity action-threshold for fee payment will be 500 μmhos in Stonecoal Branch, and 500 μmhos at the NPDES discharges to Berry Branch. If monitoring indicates an exceedance of threshold levels for more than two consecutive samples at the same location or more than three samples at the same location in a rolling 12-month period, then the applicant will incur an obligation to provide additional mitigation focused on chemical improvements within the watershed. The requirement will be reset after 24 consecutive sample reports indicate results below the threshold.

The projects to which the FCU can be applied will be defined in advance by the applicant and approved by the Corps, EPA, and any other appropriate regulatory authority. The mitigation obligation will be capped at 802 units as measured by the WV Stream and Wetland valuation metric.

If exceedances continue for more than 12 consecutive sampling periods, the applicant will retain, within 30 days, a consultant mutually agreed upon by the applicant and the Corps, EPA and any other appropriate regulatory authority. The consultant shall produce recommendations to reduce generation of dissolved solids within 120 days. The applicant shall implement the recommendations of the consultants within 45 days following written approval by the Corps, EPA, and any other appropriate regulatory authority.

APPENDIX A

Berry Branch / Stonecoal Branch
Background Surface Water Quality
Conductivity

| | TRIBUTARY | | | | | | | | MOUTH | |
| | Berry Branch | | | | | | Stonecoal | | Berry | Stonecoal |
	122	BB-5	BB-4	121	BB-3	BB-2	SB-6	SB-4	BWQ-119	SB-1
13-Feb-05		37.8	43.7	51.4	45.1	46.1			95.4	47.0
24-Feb-05	49.6						46.9	45.8		
5-Mar-05	47.6	38.8	43.1	49.3	44.0	45.2	61.2	44.6	77.2	45.0
30-Mar-05	49.0					47.2	46.9	46.2		
26-Apr-05	49.2	39.1	46.2	49.8	45.8	48.6	46.8	46.3	79.1	49.2
28-May-05	55.0	37.0		68.0		47.0	43.6	43.0	230.0	46.0
20-Jun-05							40.1	36.2		
23-Jun-05	67.6			94.0					435.0	
16-Jul-05	70.6			110.0			44.0	48.0	370.0	72.0
2-Aug-05	68.5			106.0			52.0	41.5		71.3
12-Sep-05	102.0			150.0			51.3	66.8		
4-Oct-05	119.0									
5-Oct-05				179.0						
21-Oct-05									400.0	
2-Nov-05	79.0			110.0				47.0		112.0
8-Dec-05	78.0			95.0			48.0	46.0		57.0
16-Dec-05									69.0	
12-Jan-05	55.0			70.0					183.0	
17-Jan-06							44.7	44.0		45.0
8-Feb-06	43.0	35.0		55.0		40.0	41.0	40.0		45.0
15-Mar-06	44.0	37.0	43.0	50.0		44.0	46.0	44.0		50.0
7-Apr-06									397.6	
18-Apr-06	40.0	31.1	35.9	54.8	37.4	37.8				
19-Apr-06							377.0	48.0		53.0
9-May-06	53.1			62.6			44.0	43.0		50.9
20-Jun-06	120.0			180.0		43.0	44.0	37.1		43.0
6-Jul-06									288.5	
12-Jul-06	80.0			93.1			40.4	40.1		65.4
10-Aug-06	73.0			95.0			42.2	42.1		69.8
21-Sep-06				100.1						
9-Oct-06				76.1						
10-Nov-06				65.4					665.0	
20-Nov-06									1,202.0	
7-Dec-06									222.2	
8-Dec-06				65.4						
Mean	61.3	37.0	43.1	76.1	44.6	45.2	45.4	44.0	259.3	50.5
Std Deviation	23.9	2.8	3.8	38.5	3.9	3.5	78.2	6.3	302.4	17.7

APPENDIX B

Effect of Mining Direction on water quality

The currently approved SMCRA permit for the mine contemplates mining from the northwest to the southeast with the dragline pits roughly parallel to Stonecoal Branch. This approach also envisaged the placement of excess spoil into the mined through portions of Stonecoal Branch.

The recent changes to the mine plan have changed the direction of mining with the first cuts now located on the northern boundary of Berry Branch. The first action, before any dragline activity, will be to remove a strip of overburden, and associated coal, adequate to allow the dragline to dispose of the excess spoil from the first cut. This initial strip will be excavated using a shovel / truck fleet.

It is important to note that the coal seams within the permit area dip to the northwest and that the lowest seam proposed for mining is below the elevation of Stonecoal Branch at the location of the final pit.

At all times of mining any water falling onto the area will be directed into the mining pits. the sources of water will consist of:

- drainage from upland flow within the Berry Branch watershed, which will follow the pre-mining flow paths, until it is intercepted by the active mining area
- precipitation onto the active mining area
- precipitation and groundwater inflow into the previously mined pits, some of which will result in runoff to the south to the sediment control structure along Berry Branch; the remainder of which will migrate through the backfill until it intercepts the floor of the bottom mined out coal seam. It will then flow along the pavement until it discharges into the active mining area.

Based on these flow paths the majority of the water will accumulate in the base of the active mining pits and will not discharge through the sediment control structures. The water will be removed either by natural evaporation or though seepage into the coal seam. It is possible that some water will be pumped into the sediment control structures along Berry Branch.

Any pumped flow can be monitored for water quality prior to discharge and, as it is a controlled discharge (due to pumping), it can be stopped if there are any quality concerns.

The major contributor of dissolved solids is the flow of water through spoil prior to discharge. This is reduced by landforming and contemporaneous revegetation of the regraded area in order to increase runoff rather than infiltration. It is important to eliminate large flat areas where there is a potential for infiltration. In the proposed configuration any water infiltrating the backfill will discharge into the active pit rather than to a discharge point.

For the water accumulating in the pit, it will seep into the coal seams, which are natural aquifers. As these dip to the Northwest and do not outcrop this water should not discharge.

The dip of the coal seam and the layout of the active mining pits create the opportunity for retaining water in-pit, which has the added benefit of accumulating any stormwater peaks, thus attenuating any peak flows to the receiving streams.

The ponds located on the south side of Stonecoal Branch will intercept the runoff from the regraded mine area, but they will not receive any base flow contribution from water infiltrating into the backfill, as this will have flowed through the spoil until it intercepts the basal coal seam, which is below the elevation of the creek.

Surface Mine 44
DSBB (119/UBB)
Description
DOWNSTREAM BERRY BRANCH (Mouth of Berry Branch Upstream of WV1017225 outlet)

Sample Point DSBB 119 - 12-month Trend
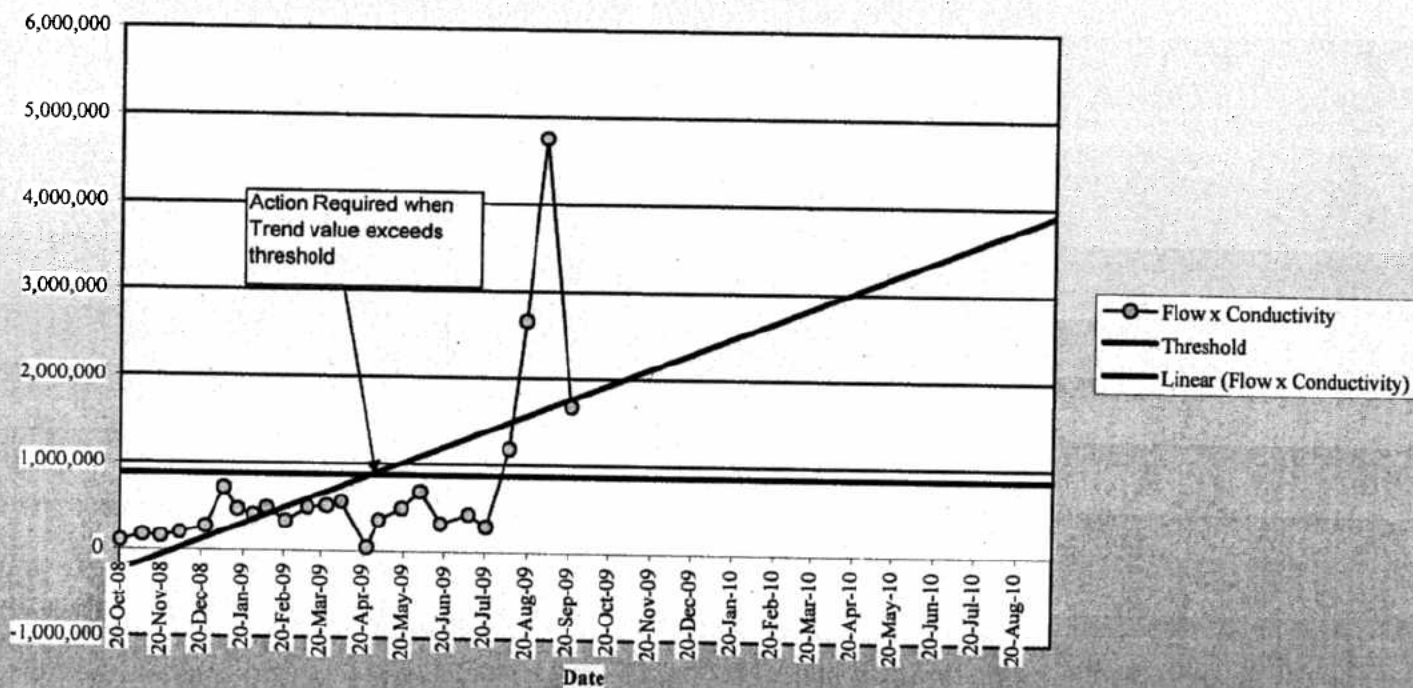
Date Sampled	Flow	Flow Units	Flow	Specific Conductance	Flow x Conductivity	Threshold		Previous 12 month data
			GPM	UMHOS				
9/16/10								
9/1/10								
8/17/10								
8/2/10								
7/18/10								
7/3/10								
6/18/10								
6/3/10								
5/19/10								
5/4/10								
4/19/10								
4/4/10								
3/20/10								
3/5/10								
2/18/10								
2/3/10								
1/19/10								

Date							
1/4/10							
12/20/09							
12/5/09							
11/20/09							
11/5/09							
10/21/09							
10/6/09							
9/21/09	1,963.0	GPM	1,963	853	1,674,439	872,808	1,674,439
9/1/09	3,690.0	GPM	3,690	1,290	4,760,100	872,808	4,760,100
8/18/09	3,800.0	GPM	3,800	700	2,660,000	872,808	2,660,000
8/6/09	2,205.0	GPM	2,205	539	1,188,495	872,808	1,188,495
7/20/09	397.0	GPM	397	728	289,016	872,808	289,016
7/7/09	556.0	GPM	556	771	428,676	872,808	428,676
6/16/09	635.0	GPM	635	500	317,500	872,808	317,500
6/1/09	3,011.0	GPM	3,011	227	683,497	872,808	683,497
5/18/09	878.0	GPM	878	558	489,924	872,808	489,924
5/1/09	878.0	GPM	878	403	353,834	872,808	353,834
4/22/09	1,272.0	GPM	1,272	34	43,248	872,808	43,248
4/3/09	2,206.0	GPM	2,206	256	564,736	872,808	564,736
3/23/09	3.4	CFS	1,544	334	516,305	872,808	516,305
3/9/09	3.2	CFS	1,432	345	494,246	872,808	494,246
2/20/09	2.1	CFS	943	355	334,509	872,808	334,509
2/6/09	3.1	CFS	1,391	351	487,815	872,808	487,815
1/27/09	1.6	CFS	736	552	406,317	872,808	406,317
1/15/09	2.5	CFS	1,113	419	466,611	872,808	466,611
1/5/09	3.1	CFS	1,382	517	714,699	872,808	714,699
12/22/08	1.3	CFS	588	458	268,995	872,808	268,995
12/3/08	0.7	CFS	305	646	197,162	872,808	197,162
11/19/08	0.4	CFS	189	800	150,807	872,808	150,807
11/5/08	0.5	CFS	220	759	166,924	872,808	166,924
10/20/08	0.3	CFS	139	721	100,318	872,808	100,318
10/7/08	0.4	CFS	171	709	120,924	872,808	
10/1/08	0.7	CFS	305	684	208,760	872,808	
9/24/08	0.2	CFS	90	740	66,427	872,808	
9/15/08	0.7	CFS	292	709	206,843	872,808	
8/26/08	0.4	CFS	184	716	131,759	872,808	
8/14/08	1.0	CFS	431	760	327,466	872,808	
7/30/08	0.7	CFS	328	692	226,731	872,808	
7/18/08	1.5	CFS	673	565	380,383	872,808	
7/10/08	6.0	CFS	2,702	287	774,921	872,808	
7/2/08	1.5	CFS	660	453	298,550	872,808	
6/26/08	1.1	CFS	507	653	331,187	872,808	
4/2/08	1.3	CFS	583	226	132,100	872,808	
1/4/08	0.3	CFS	148	1,333	197,436	872,808	
10/2/07	59.0	GPM	59	499	29,441	872,808	
9/18/07	65.0	GPM	65	418	27,190	872,808	
8/18/07	287.0	GPM	287	477	136,956	872,808	
8/10/07	100.0	GPM	100	438	43,800	872,808	
7/17/07	43.0	GPM	43	594	25,542	872,808	
7/3/07	106.0	GPM	106	511	54,166	872,808	
6/19/07	120.0	GPM	120	434	52,128	872,808	
6/5/07	5,043.0	GPM	5,043	1,129	5,693,547	872,808	
5/18/07	4,663.0	GPM	4,663	1,125	5,245,875	872,808	

5/3/07	4,152.0	GPM	4,152	1,272	5,281,344	872,808	
4/20/07	4,921.0	GPM	4,921	111	545,739	872,808	
4/5/07	3,263.0	GPM	3,263	212	691,756	872,808	
3/21/07	259.0	GPM	259	378	97,954	872,808	
3/5/07	357.0	GPM	357	622	222,054	872,808	
2/20/07	3,673.0	GPM	3,673	423	1,552,577	872,808	
2/5/07	5,108.0	GPM	5,108	1,640	8,377,120	872,808	
1/18/07	4,322.0	GPM	4,322	495	2,139,390	872,808	
1/6/07	3,214.0	GPM	3,214	510	1,639,140	872,808	
12/21/06	2,482.0	GPM	2,482	1,348	3,345,736	872,808	
12/7/06	3,325.0	GPM	3,325	222	738,815	872,808	
11/20/06	3,352.0	GPM	3,352	1,202	4,029,104	872,808	
11/15/06	941.0	GPM	941	131	122,895	872,808	
10/9/06	3,563.0	GPM	3,563	665	2,369,395	872,808	
10/9/06	1,224.0	GPM	1,224	144	176,623	872,808	
7/6/06	2,992.0	GPM	2,992	289	863,192	872,808	
4/7/06	4,115.0	GPM	4,115	398	1,636,124	872,808	
1/12/06	2,815.0	GPM	2,815	183	515,145	872,808	
12/16/05	23.1	CFS	10,355	69	714,461	872,808	

Threshold Calculation			1,746	500	872,808

1	cfs	=	448.83	gpm

DEC 1 4 2010

Colonel Keith A. Landry, District Engineer
Louisville District Corps of Engineers
Attn: Lee Anne Devine (Regulatory Branch)
OP-FN, Room 752
P.O. Box 59
Louisville, Kentucky 40201-0059

Subject: Leeco, Inc., Stacy Branch Mine
       U.S. Army Corps of Engineers LRL-2007-0217
       Kentucky Division of Mine Permits (KDMP) #897-0480

Dear Colonel Landry:

       The U.S. Environmental Protection Agency (EPA), Region 4, has completed its review of Leeco, Inc.'s proposed Stacy Branch surface coal mining project (LRL-2007-0217) in Perry and Knott Counties, Kentucky. Our review included the most recent version of the U.S. Army Corps of Engineers (Corps) Clean Water Act (CWA) Section 404 permit application (on a CD dated March 4, 2010, which includes information originally submitted to KDMP as Surface Mining Control and Reclamation Act (SMCRA) permit application #897-0480); information submitted to KDMP with subsequent SMCRA permit amendments; supplemental mitigation documents obtained electronically on April 8, 2010, and further mitigation documents provided to staff in meetings on November 2, 2010 and November 5, 2010; supplemental information dated April 27, 2010 (including a Fill Placement Optimization Process engineering analysis); additional application amendments received by email on August 24, 2010; and two sets of supplemental information received by email on November 4, 2010, and on November 24, 2010.

       This review was conducted in accordance with the Enhanced Coordination Procedures (ECP) for surface coal mining applications as detailed in the June 11, 2009 *Memorandum of Understanding among the U.S. Department of Army, U.S. Department of Interior and the U.S. Environmental Protection Agency Implementing the Interagency Action Plan on Appalachian Surface Coal Mining*. The purpose of this letter is to present EPA's project-specific comments and recommendations, including recommended special permit conditions that EPA believes are necessary to ensure compliance with the requirements of our regulations pursuant to the CWA Section 404(b)(1) Guidelines ("Guidelines"; 40 C.F.R. Part 230). The 60-day period for ECP coordination was initiated by your staff on September 16, 2010, and has been extended by mutual agreement to conclude on December 14, 2010.

       As described below, EPA has significant environmental and water quality concerns with this project as currently proposed. Given the project's significant proposed impacts, including six valley fills resulting in more than four miles of permanent stream impacts, anticipated

downstream water quality effects, and associated impacts to aquatic wildlife, we believe that significant changes are needed before the project will comply with the Section 404(b)(1) Guidelines and be appropriate for permit issuance. EPA's recommended changes include:

- Requiring additional analyses to justify that avoidance of one or more valley fills proposed by the applicant is not possible, given analyses to suggest that their volume is not needed for placement of excess spoil;
- Requiring additional robust BMPs as part of construction and operation of the mine to reduce anticipated water quality impacts;
- Phasing construction of valley fills to monitor effectiveness of BMPs and to assure that initial fills represent a significant reduction in the proportion of total anticipated stream impacts from the project;
- Requiring that authorization of subsequent phases of the mining operation be contingent upon demonstrating that discharges from the operation do not cause or contribute to elevated conductivity levels associated with violations of water quality standards or cause significant degradation to streamlife;
- Conducting downstream water quality and biological monitoring to effectively assess mining impacts to downstream water quality and wildlife;
- Modifying the mitigation plan if necessary to ensure that the lost structure and function of impacted resources are being fully compensated; and
- Adequately assessing and addressing cumulative impacts of the proposed project, including environmental justice considerations.

EPA believes these improvements to the CWA Section 404 permit are necessary to ensure the project meets the requirements of the CWA and the agencies' implementing regulations, including the Section 404(b)(1) Guidelines.

Project Overview

The CWA Section 404(b)(1) Guidelines promulgated by EPA in conjunction with the Secretary of the Army establish the substantive environmental standards for proposed discharges of dredged or fill material in waters of the United States. The Guidelines establish a sequence of review requiring: (1) an evaluation of all practicable alternatives that meet the project's basic purpose to ensure that only the Least Environmentally Damaging Practicable Alternative is permitted; (2) taking all appropriate and practicable steps to minimize potential adverse impacts; and (3) compensating for all remaining unavoidable impacts to aquatic resources. In addition, the Guidelines require that no discharge may be permitted that would cause or contribute to significant degradation of waters of the United States. The Guidelines form the basis of our review of this permit application, and we have highlighted particularly relevant provisions below.

Leeco, Inc.'s proposed Stacy Branch project was placed on the final list of applications subject to the ECP on September 30, 2009, due to environmental concerns regarding avoidance and minimization, compensatory mitigation, cumulative impacts, and the potential for downstream water quality impacts. The proposed project is a new surface coal mine that would conduct contour, auger, and area mining operations over 869 acres. The project area straddles the eastern Perry County-southwestern Knott County boundary in Kentucky. It was originally

permitted by KDMP under Permit #897-0480 on June 6, 2007, a permit that has been subsequently amended several times. Leeco has requested authorization to construct six valley fills and six temporary sediment control ponds that would permanently impact 22,861 linear feet (lf) of streams, or 4.3 miles (5,914 lf of intermittent and 14,807 lf of ephemeral streams). These streams are tributaries to Stacy Branch, Yellow Creek and Sugar Creek. Sediment ponds proposed beneath the six valley fills would impact an additional 2,140 lf of intermittent stream reaches.

Alternatives Analysis – 40 CFR § 230.10(a)

The Section 404(b)(1) Guidelines, (Guidelines) 40 CFR § 230.10(a), provide that no discharge of dredged or fill material shall be permitted if there is a practicable alternative to the proposed discharge that would have less adverse impact on the aquatic ecosystem. The Guidelines require consideration of project alternatives to eliminate and/or reduce the number of discharges of dredged or fill material occurring in the waters of the United States. Only the Least Environmentally Damaging Practicable Alternative (LEDPA) may be permitted. To identify the LEDPA, a full range of practicable alternatives that would avoid and minimize impacts to aquatic resources must be evaluated. When evaluating permit applications in light of this provision, key factual considerations should include the adequacy of the alternatives analysis submitted, the number and size of valley fills, the number and extent of streams to be impacted, the nature of downstream water quality impacts (including impacts to aquatic wildlife), and the number and location of sediment ponds.

To supplement the original alternatives analysis included in the CWA Section 404 permit application, the applicant has submitted a Fill Placement Optimization Process (FPOP) analysis following Kentucky Reclamation Advisory Memorandum (RAM) 145. This analysis calculates the maximum stream impact allowable under present Commonwealth guidelines by optimizing placement of excess spoil material. As described in the applicant's analysis, the Stacy Branch project has minimized its impacts to waters of the United States consistent with FPOP and operational constraints. The applicant twice submitted additional information on practicability of alternatives, which was received by EPA on November 4, 2010, and November 23, 2010.

EPA appreciates the FPOP avoidance and minimization analysis submitted by the applicant and the company's efforts to avoid and minimize impacts using this process. However, EPA has concerns that the applicant has not appropriately evaluated opportunities to avoid constructing one or more of the six valley fills it has proposed. For example, the applicant justifies the need for valley fill #7 based in part on the proposed mining sequence and on an assumption that haul distances greater than ½-mile are infeasible. Another example is valley fill #5, which as proposed would contain less than 2 percent of the overall spoil volume proposed for placement in valley fills (205,951 yd^3 of 11,055,218 yd^3).

EPA believes that the applicant's additional analysis of avoiding one or more fills is not sufficient to determine practicability, and the applicant should further evaluate avoidance of one or more valley fills. EPA does not believe that constraining haul distances to ½ mile is a sufficient justification for demonstrating that a specific valley fill is operationally necessary. Also, avoiding valley fill #5 would preserve the highest quality stream on the project site, as

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measured by its low levels of specific conductance. This would help ensure that this stream continues to contribute dilution water to the watershed.

In addition to up-front avoidance of at least one additional valley fill, we recommend that the Corps work with the company and the State after initial phases of mining are completed to compare coal tonnage actually being mined, spoil generation rates, and the amount of spoil stored in valley fills with permitted levels to assess whether approved spoil volumes are being generated and to reevaluate excess spoil storage requirements. EPA also believes that fill compaction proposed by the applicant as a Best Management Practice (BMP) may further reduce the need to place spoil in one or more valley fills on the project site. If the permittee is successful in optimizing fill placement such that one or more valley fills is not necessary, or if the Corps determines that the permittee's analysis is insufficient or not compelling, EPA believes that the permit should require that any unfilled valley(s) be protected by a permanent conservation easement to ensure that the preserved stream continues to provide dilution water to the watershed.

"Compliance with Other Environmental Standards" – 40 CFR § 230.10(b) and "Significant Degradation" – 40 CFR § 230.10(c)

The Section 404(b)(1) Guidelines, 40 CFR § 230.10(b), provide that no discharge may be permitted that would cause or contribute to a violation of any applicable water quality standard, violate any applicable toxic effluent standard, or jeopardize the existence of threatened or endangered species. When evaluating permit applications in light of this provision, key factual considerations should include the pre-mining water quality and potential for water quality impacts downstream of proposed sediment ponds, including impacts from selenium, conductivity, pH, turbidity, dissolved solids, and manganese; the potential impacts to biotic integrity as a result of water quality degradation; and impacts to threatened and endangered aquatic species.

A growing body of scientific evidence demonstrates that certain pollutants or pollutant parameters associated with coal mine discharges are causing or contributing to violations of narrative water quality standards.[1] Recent studies have shown that there is a direct correlation between stream impairment and discharge of total dissolved solids (TDS)/specific conductance (SC, or conductivity) due to Appalachian surface coal mining. As described in the *Cumulative Impact Assessment—North Fork Kentucky River Watershed* submitted with the applicant's Section 404 permit application, the native biotic communities in Stacy Branch have previously

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[1] On April 1, 2010, EPA released two Office of Research and Development (ORD) reports: *The Effects of Mountaintop Mines and Valley Fills on Aquatic Ecosystems of the Central Appalachian Coalfields* and *A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams*. The ORD reports have been submitted to the EPA Science Advisory Board (SAB) for review and are also publicly available. In the interim, EPA views the reports as providing information, along with published, peer-reviewed scientific literature, that may inform permit reviews.

Based on the best information available to EPA, projects with predicted specific conductance (conductivity) values below 300 µS/cm generally are not likely to cause water quality violations or significant degradation of the aquatic ecosystem, at least not based on conductivity alone. Discharges with levels of conductivity above 500 µS/cm generally are likely to be associated with adverse impacts that could cause or contribute to significant degradation and/or excursions from narrative water quality criteria.

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been degraded by mining, with Macroinvertebrate Biotic Index (MBI) scores at four Stacy Branch stations measured as poor or very poor.

EPA believes the Kentucky Pollutant Discharge Elimination System (KPDES) General Permit (KYG046177; effective July 23, 2007) issued for this project does not adequately protect water quality, including long-term and cumulative effects on downstream water quality. Prior to issuing the KPDES general permit, the Commonwealth did not conduct any Reasonable Potential (RP) analysis or calculate any numeric effluent limitations for total dissolved solids or other mining-associated pollutants to ensure compliance with water quality standards. EPA believes that additional water quality-related permit conditions should be required as part of the Section 404 permit to ensure that water quality criteria and designated uses are protected.

The Section 404(b)(1) Guidelines, 40 CFR § 230.10(c), provide that no discharge shall be permitted that will cause or contribute to significant degradation of the waters of the United States. When evaluating permit applications in light of this provision, key factual assessments should include all direct, indirect, and cumulative adverse effects of the proposed mine in consideration of current, previous and reasonably foreseeable future impacts; a watershed assessment of total length of streams to be impacted and/or total area of valley fills in waters of the United States; the extent of streams to be impacted, including extent of impacts to critical headwater streams and/or perennial reaches; the geographic location of the proposed mine; and an assessment of impacts based on a watershed-scale evaluation of stream quality, water temperature, stream diversity, and other relevant factors.

To protect water quality and prevent significant degradation of waters of the United States, EPA recommends that the following principles be incorporated within the Section 404 permit issued for the Stacy Branch project. While the applicant has taken steps to incorporate several of the practices described below within the mining plan, EPA believes that additional actions are necessary to protect receiving waters from further elevation of pollutants or pollutant parameters and to prevent significant degradation of downstream waters. These actions include more robust best management practices, sequencing of valley fill construction, adaptive management actions that may be necessary based on water quality and biological monitoring, and monitoring and remediation of cumulative watershed impacts. Detailed proposed Special Conditions for implementing these recommendations are included in Enclosure 1 (Recommended Special Permit and Monitoring Conditions), and Enclosure 2 (Adaptive Management Plan Timelines).

<u>Use of Best Management Practices</u>

Based on the scientific information described above, EPA is concerned that the project is likely to cause or contribute to violations of applicable water quality standards and result in significant degradation of the aquatic environment. EPA's key concerns relate to the project's likelihood of further elevating total dissolved solids in streams already impacted by previous mining practices. To help address these concerns, the applicant has identified specific construction practices and mining operation improvements (or Best Management Practices (BMPs)), associated with the placement of fill material into waters of the United States, that are intended to reduce the likelihood of further elevating mining-related pollution in downstream receiving waters. These BMPs are laid out in Enclosure 1 (Recommended Special Permit and

Monitoring Conditions). EPA appreciates the applicant's willingness to implement these BMPs and believes these BMPs are necessary operational improvements to the mine and should be included as requirements in the Corps permit.

Due to the significant scale of the proposed project and uncertainty regarding BMP effectiveness, EPA believes that additional BMPs should be implemented immediately in order to reduce the likelihood that water quality problems will occur. Such BMPs could include taking further steps to minimize water infiltration into fill material using synthetic caps or liners, promoting diffuse discharges to mimic forested watersheds using techniques such as weep berm-forest passive treatment systems, and utilizing the Forest Reclamation Approach (FRA). EPA recommends that these BMPs be implemented immediately. EPA would strongly support efforts by the applicant to obtain authorization as needed from the Office of Surface Mining Reclamation and Enforcement to use these techniques as SMCRA Experimental Practices.

Sequencing of Valley Fill Construction

As referenced above, a substantial body of scientific information, including research conducted by EPA, has demonstrated significant downstream water quality impacts from Appalachian surface coal mining operations, particularly as a result of discharges of total dissolved solids and selenium from valley fills. In EPA's review of proposed projects, a key goal is to ensure that surface coal mining operations do not continue to cause similar long-term deleterious effects, which are difficult to remediate after mining-related discharges of fill have begun. Toward this goal, EPA believes that large-scale mining projects should be "sequenced," an approach involving phased approval of valley fills consistent with results of ongoing monitoring to assess the nature and extent of environmental impacts and the effectiveness of BMPs in reducing these impacts. Under this approach, additional valley fills may only be approved where monitoring demonstrates that previously authorized discharges are fully consistent with applicable requirements of the law.

For this proposed project, EPA appreciates that the applicant has submitted analyses describing the potential for phasing of the proposed project (analyses received November 4, 2010, and November 23, 2010). The applicant proposes to initially construct fills 4, 3, and 2 which would impact 75 percent of the total length of streams proposed to be impacted by the mine, and to construct the remaining three fills (5, 6, and 7) "as encountered." The applicant further proposes that no more than three fills will be in construction at any time. During construction, the applicant proposes to monitor the effluent of the ponds below each fill for conductivity, and to develop and undertake an AMP if water quality problems occur.

While EPA appreciates the applicant's phasing analysis, EPA remains concerned that the applicant's proposal would result in immediate authorization of discharges to 75 percent of the total linear footage of waters of the U.S. proposed to be impacted on the project site. These impacts are likely to be irreversible. EPA believes the initial approval of valley fills should represent a significantly lower percentage of total anticipated impacts, and that no additional discharges be approved until an assessment of the water quality and biological effects is completed. EPA recommends that no more than two valley fills should be under construction at one time, including no more than one of the three largest fills (3, 4 and 6). While other surface coal mining projects have successfully demonstrated the ability to fully sequence fill

construction (one at a time), in this case EPA believes that the applicant's willingness to implement BMPs that prescribe sequential lift fill construction with minimal ground disturbance outside the lift under construction makes more than one concurrent fill (but no more than two fills) operationally necessary. Given the nature and extent of anticipated water quality and environmental impacts associated with the mine and the operational and engineering considerations identified by the applicant, we believe this approach is appropriate and consistent with the requirements of the law.

Adaptive Management

Due to significant uncertainty regarding the water quality effects of the BMPs described above, EPA believes that adaptive management is critical to addressing and thereby preventing irreversible downstream water quality impacts. Baseline conductivity levels in streams to be affected by the proposed project exceed levels associated with healthy aquatic communities in central Appalachian streams. To address the potential for the project to cause significant degradation or exacerbate existing downstream water quality impacts, the applicant has proposed an Adaptive Management Plan (AMP) that identifies specific actions to be undertaken to ameliorate such effects. The applicant has proposed that conductivity of 500 µS/cm or background conductivity,[2] whichever is greater, in streams below valley fills, be included in the Special Permit Condition for triggering remedial action (referred to in the applicant's supplemental response as "the conductivity threshold"). Monitoring in streams showing conductivity levels that approach or exceed the conductivity threshold following initial fill construction would require the applicant to implement additional BMPs to address water quality concerns. The applicant has proposed an approach with up to two phases of AMP actions to be undertaken if water quality monitoring continues to exceed the conductivity threshold.

While EPA recognizes that the applicant's proposed AMP is a significant step forward, EPA believes that the Corps permit should not authorize further discharges until conductivity levels in streams below mining remain consistently below levels that current research demonstrates are inconsistent with applicable narrative water quality standards and significant degradation of the aquatic environment. EPA believes that Special Permit Conditions should require AMPs to ensure that effluent conductivity levels do not exceed 500 µS/cm, and in-stream conductivity levels do not exceed 500 µS/cm or increase above current background levels if levels are already above 500 µS/cm. Therefore, EPA believes that monthly average flow-weighted effluent conductivity trends or two consecutive measurements that exceed 500 µS/cm in any pond's effluent (as defined in Recommended Special Permit Condition I.E.), should trigger a requirement for an effluent AMP. Similarly, monthly average in-stream conductivity trends or two consecutive measurements that exceed 500 µS/cm or background in any stream (as defined in Recommended Special Permit Condition I.F.), should trigger a requirement for a stream AMP. If, after two rounds of adaptive management under either the effluent or the stream AMP, monthly flow-weighted average effluent conductivities remain above 500 µS/cm, or in-

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[2] Background conductivity for the streams associated with each hollow fill is proposed to be equal to the maximum value among that data available for each stream, as summarized in Table 1 in the document "Stacy Brach [*sic*] Supplemental Response - EPA Comment Letter I (1).pdf" received November 23, 2010. As summarized by the applicant, three streams are currently below 500 µS/cm (those associated with fills 5, 6, and 7), while three streams are above 500 µS/cm (those associated with fills 2, 3, and 4). EPA disagrees with using the maximum of each stream's available data to define the background condition.

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stream conductivities remain above 500 μS/cm or background, then the permittee should immediate cease discharges of fill material into waters of the U.S., unless required for reclamation of any open fills, until both effluent and in-stream conductivity falls below 500 μS/cm (as defined in Recommended Special Permit Conditions I.E. and I.F.). If either of these scenarios occurs, the applicant could implement additional BMPs or could undertake actions that reduce, treat, or eliminate discharges of water from fills or reclaimed lands into the affected receiving waters. If these actions reduced effluent and in-stream conductivity levels below 500 μS/cm, mining activities could continue and additional fills could be authorized. Actions that we propose for consideration within these AMPs are outlined in Enclosure 1 (Recommended Special Permit and Monitoring Conditions).

<u>Cumulative Water Quality Effects</u>

The applicant's *Cumulative Impact Assessment—North Fork Kentucky River Watershed* identified existing water quality and biological impacts to streams in the watershed. Many of these impacts are likely a result of past and/or ongoing surface coal mining activities. EPA is concerned that the proposed project may further exacerbate these impacts by reducing the existing contribution of clean water from streams on the project site to downstream waters. Such dilution may be reduced at a watershed level even if individual streams on the project site remain below 500 μS/cm.

To address this concern, EPA believes that the AMP should also require monitoring of conductivity levels downstream of the proposed operation in Stacy Branch, Sugar Creek, and Yellow Creek, commencing upon authorization of activities at the project site. Several months of monitoring data should be collected to establish a baseline conductivity level against which future project impacts will be evaluated. If the baseline conductivity level is below 500 μS/cm before the mining project begins, action under the AMP should be triggered if monitoring shows that conductivity exceeds 500 μS/cm as a result of the project. If the baseline conductivity level exceeds 500 μS/cm before the mining project begins, then action under the AMP should be triggered if monitoring shows a net increase in conductivity levels from this baseline as a result of this project.

Compensation for Unavoidable Impacts – 40 CFR § 230.91

EPA is concerned that the proposed compensatory mitigation plan for this project is inadequate in its current form. To ensure that this project complies with the Section 404(b)(1) Guidelines, EPA recommends that the Corps address the following issues:

- Discrepancies between stream assessments conducted by EPA and those conducted by the applicant, including missing documentation from the applicant to justify its conclusions that streams to be impacted are of low quality;
- Concerns over the temporary nature of sediment pond impacts (which your staff have acknowledged are not temporary); and
- Concerns over use of Tates Pond and Spring Branch mitigation projects due to potential downstream water quality concerns and use of Nationwide Permit 27 as a de facto mitigation bank.

Discrepancies Among Stream Assessments

Mitigation requirements calculated for this project are based on the applicant's stream assessments performed using the Eastern Kentucky Stream Assessment Protocol (EKSAP). EPA has concerns regarding the EKSAP Ecological Integrity Index (EII) scores, and in particular the Rapid Bioassessment Protocol (RBP) component, as calculated by the applicant. In particular, EPA is concerned that these scores may underestimate stream quality and therefore lead to inadequate compensatory mitigation.

To help inform EPA's evaluation of the Stacy Branch project, EPA Region IV conducted site visits to spot-check the applicant's assessments, and assessed stream conditions at one location below each proposed valley fill. Although EPA did not assess stream reaches in precisely the same locations as the applicant, the Agency did assess segments comparable to the pond segments assessed by the applicant's EII determination. EPA's spot checks were in the applicant's assessed stream segments. In the course of its evaluation of the applicant's data, EPA learned that complete documentation of the applicant's assessments is unavailable, including the raw data on stream segments of differing condition that were averaged to determine the overall condition of each affected stream reach.

A comparison between EPA's and the applicant's data suggests that the applicant's stream assessments could be inaccurately low and therefore the proposed compensatory mitigation may be inadequate. Because the EKSAP assigns compensatory mitigation requirements partly in proportion to RBP habitat scores, these disparities in assessment scores result in similar differences in calculated compensatory mitigation requirements. EPA recommends that the applicant reevaluate the streams on site and provide complete documentation to the agencies to support the EII calculations. If these revised calculations do not demonstrate that the current compensatory mitigation proposal will adequately compensate for lost stream functions, additional mitigation should be required to offset these impacts and prevent significant degradation.

Compensation for Non-Temporary Sediment Pond Impacts

In discussions with your staff and the applicant, we have noted that some impacts associated with sediment ponds that were originally described by the applicant as "temporary" (totaling 2,140 lf of intermittent stream) would not be temporary, but instead would last 10 years or more. EPA considers such duration to be beyond any reasonable interpretation of the term "temporary," and believes that these impacts should be mitigated contemporaneously with the impacts themselves. Your staff has verbally agreed that these impacts require additional contemporaneous mitigation.

In response to concerns expressed by EPA and your staff, the permittee has proposed to provide the additional compensatory mitigation in the form of additional credits from the Spring Branch watershed project described below. We appreciate your staff's efforts to require additional compensatory mitigation to compensate for these non-temporary impacts, but we have concerns with use of the Spring Branch watershed project as described below.

Inappropriate Use of Nationwide Permit 27 Authorization

As part of the applicant's compensatory mitigation plan, the applicant proposes to make in-lieu fee payments to the Kentucky Department of Fish and Wildlife Resources Wetland and Stream Mitigation Program for ephemeral stream impacts. For intermittent streams, the applicant proposes to mitigate for impacts by removing an existing sediment pond (Tates Pond in Pidgeonroost Hollow, Perry County, KY), and using compensatory mitigation credits from Nationwide Permit (NWP) 27 authorization LRL-2008-738 (associated with the Spring Branch watershed in Wolfe County, KY). EPA staff has visited the proposed Tates Pond and Spring Branch compensatory mitigation sites, and believe they will provide the appropriate kind of compensatory mitigation for the loss of ephemeral and intermittent stream functions associated with the proposed mining project. However, EPA has concerns with each of these projects as a source of compensatory mitigation credits.

Tates Pond is adjacent to an apparent side-hill fill that may be the result of pre-law mining activity. The pond effluent pH at the time of EPA's visit was low (4.2). Given this low pH, EPA is concerned that this compensatory mitigation project may result in transport of acidic water downstream, which may degrade downstream waters and offset any benefits from removing Tates Pond. EPA recommends that the Corps require the applicant to modify this site's design to address the low pH, and to develop compensatory mitigation performance criteria that will ensure that the proposed compensatory mitigation does not cause or contribute to downstream water quality problems.

With respect to the Spring Branch project, EPA understands that the Spring Branch watershed project is not an approved mitigation bank. EPA further understands that the NWP 27 was applied for prior to the issuance of the April 10, 2008, Compensatory Mitigation for Losses of Aquatic Resources Final Rule (40 CFR Part 230 Subpart J and 33 CFR Part 332) and recognizes that this project is intended to provide compensation for multiple CWA Section 404 permits, including the Stacy Branch project. Given this, EPA believes that the Spring Branch project is effectively operating as a private (single user) compensatory mitigation bank. This practice is not in keeping with the goals of the 2008 compensatory mitigation rule or compensatory mitigation guidance, and does not adequately ensure that the work done under the NWP 27 will not be counted as compensatory mitigation for multiple impacts. EPA recommends that the work done in the Spring Branch watershed be considered as compensatory mitigation for the Stacy Branch project alone. Alternatively, EPA recommends that the applicant apply to the appropriate Interagency Review Team (IRT) for approval to operate as a compensatory mitigation bank which could then sell or transfer credits consistent with Clean Water Act regulations.

Determination of Cumulative Effects on the Aquatic Ecosystem – 40 CFR § 230.11(g)

The Section 404(b)(1) Guidelines, 40 CFR § 230.11(g), provide that cumulative effects attributable to the proposed project should be predicted to the extent reasonable and practicable, including the collective effects of any foreseeable future discharges in the same watershed, whether by the applicant alone or in combination with others. The Corps is required to collect and solicit information about cumulative effects on aquatic ecosystems, and to consider this information in evaluating the proposed permit. As noted earlier, the applicant has provided the *Cumulative Impact Assessment—North Fork Kentucky River Watershed*, which includes an

assessment of the Stacy Branch watershed. It is our understanding that the Corps will rely on these assessments for this permit decision.

While we appreciate the applicant's efforts, we are concerned that the assessment for the North Fork Kentucky River watershed, based on an eight-digit hydrologic unit code (HUC8), may be at a scale too large to provide a meaningful analysis of impacts from mining. We believe it is more appropriate to use a smaller geographic scope, as was done for the Stacy Branch watershed (HUC12), for making permit decisions. EPA's preliminary analysis indicates that as much as 23 percent of the Montgomery Creek-Carr Fork watershed (HUC12) has already been mined, indicating the cumulative impacts to this watershed from mining may already be resulting in water quality inconsistent with Kentucky standards. In addition, we have significant concerns over the quality of the analyses for both of the applicant's assessments, and are not confident that many of the conclusions are well supported. Moreover, we are concerned that the analyses do not address potential human health impacts, including potential impacts to private drinking water wells and other drinking water supplies. We also believe the analyses should consider, at a minimum, the ecosystem function and habitat, and the effects of the hydrologic modifications to the sub-basin and subwatersheds, as well as address the impact of deforestation and development on water quality, water quantity and other ecological conditions. We also believe the cumulative impact assessment should expand upon its baseline assessment to account for reasonably foreseeable impacts upon the resource caused by the proposed action and other anticipated actions occurring within the immediately impacted watershed and the downstream receiving watershed. We would appreciate the opportunity to discuss these issues with you in more detail, both for this particular permit application and as a more general approach to evaluating cumulative impacts for future permit applications.

Environmental Justice

Consistent with Executive Order 12898 ("Federal Actions to Address Environmental Justice in Minority Populations and Low-income Populations") and the accompanying Presidential Memorandum, EPA recommends that the Corps analyze the potential for disproportionately high adverse human health or environmental effects on low-income populations in the area. EPA appreciates that the applicant has submitted supplemental information including an Environmental Justice (EJ) analysis to the Corps (received by EPA on November 24, 2010). This analysis includes a characterization of the economic status of residents in Vicco, as well as Perry and Knott counties, and clearly identifies EJ communities near the proposed mine. However, EPA believes that the analysis does not adequately address several EJ concerns.

EPA recommends better quantification of effects on EJ communities, including impacts from blasting, truck traffic, noise, fugitive dust, and habitat loss. For example, the applicant's analysis does not clearly describe how potential structural damage to nearby residences from blasting would be avoided. We also recommend that an assessment of how property values may be impacted by mining activity is important to better understand the socio-economic effects of the proposed project, recognizing that economic well-being is one of the most important social determinants of health. Additional consideration should be given to the potential impacts of these activities on subsistence fishing, hunting, foraging, and gardening in the areas within and/or adjacent to the proposed permit boundary in order to protect these cultural and economic

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values. Additional information is also needed concerning sources of drinking water for affected populations (including municipal water supplies and private sources of drinking water including streams and/or wells).

EPA also recommends that the Corps take steps to ensure meaningful engagement of affected communities in the permitting and NEPA process for this project. For example, we recommend that details regarding proposed modifications to the project, including the draft NEPA document, be made available to affected EJ communities for their review and comment. These outreach efforts would provide the affected communities with a clearer picture of the potential impacts of the project and assist the Corps in their decision-making process.
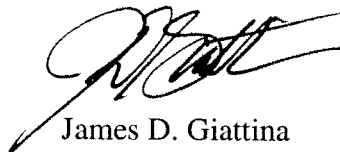
Conclusion

Modifications consistent with EPA's recommendations are needed to ensure that the CWA Section 404 permit would be consistent with the Section 404(b)(1) Guidelines. Absent modification, discharges associated with the proposed project have not been effectively avoided and minimized, would cause or contribute to violation of applicable water quality standards, would cause or contribute to significant degradation of the aquatic environment, and may not be adequately mitigated. Depending on the results of the reassessment of predicted impacts, additional compensatory mitigation may be required to compensate for lost stream functions. As described above, we have enclosed recommended special permit and monitoring conditions we believe are necessary to ensure compliance with the Section 404(b)(1) Guidelines. The absence of these improvements would render this permit a candidate for further review under CWA Section 404(c) given the nature and extent of anticipated unacceptable adverse impacts. In addition, we do not believe that the Corps can support a Finding of No Significant Impact under the National Environmental Policy Act without adopting these recommended special permit conditions, in which case we would recommend that the Corps prepare an Environmental Impact Statement.

I want to thank you and your staff for your cooperation and willingness to address our issues. We appreciate being able to work closely with you and the applicant to resolve the concerns outlined above, and hope to be able to continue to do so as necessary. If you have any questions, please call me at (404) 562-9470 or Kevin H. Miller of my staff at (404) 562-9435.

Sincerely,

James D. Giattina
Director
Water Protection Division

Enclosure 1: Recommended Special Permit and Monitoring Conditions
Enclosure 2: Adaptive Management Plan Timelines

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Enclosure 1
Recommended Special Permit and Monitoring Conditions

I.   **Recommended Special Permit Conditions**

A.   The permittee shall adhere to the plans and conditions included in the permit application submitted on a CD dated March 3, 2010 and all subsequently obtained supplemental information.

B.   The permittee shall submit a detailed plan to the U.S. Army Corps of Engineers Louisville District (Corps) and the U.S. Environmental Protection Agency, Region 4 (EPA) for implementing mine design and hollow fill construction alternatives and best management practices (BMPs) to minimize total dissolved solids (TDS) and specific conductance (SC, or conductivity) during the placement of fill material into waters of the United States (U.S.) during mining, reclamation and the construction of the hollow fills. The objective of these procedures is to ensure that mine effluent cannot reasonably be expected to cause or contribute to excursions from narrative water quality criteria and/or significant degradation, consistent with best-available science on the association between conductivity and adverse impacts to aquatic ecosystems (noted above under Footnote 1), as measured by monthly flow-weighted conductivity (see Special Permit Conditions I.E. and I.F., below). This plan must be approved by the Corps, and transmitted to EPA, prior to discharge of any dredged or fill material into any water of the U.S. Proposed actions should include, but are not necessarily limited to[3]:

General BMPs
- Existing vegetation will be retained to the extent practicable.
- Highly reactive strata units (TDS and/or sulfate producing geologic strata[4]) will be identified and isolated as part of the mining process.
- Acidic and toxic material encountered during the mining operation will be handled in accordance with the approved Toxic Materials Handling Plan in the project's SMCRA permit.
- Topsoil or topsoil substitute, as approved by the Kentucky Department for Natural Resources (KDNR) in the SMCRA permit for this project will be stockpiled and managed so that re-graded areas can be covered with a layer of topsoil or topsoil substitute and revegetated as quickly as practicable.

Hollow Fill Construction/Reclamation BMPs
- Implement hollow fill design alternatives that reduce infiltration (e.g. compact surface lifts, crown the fill surface) and controls flow through the fill to avoid contact time between water and highly reactive materials (i.e. TDS and/or sulfate producing geologic strata[4]).
- The fill will be constructed in a "bottom-up" manner with 50 foot vertical lifts.

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[3] The listed BMPs were proposed by the applicant in supplemental materials received by EPA on November 4 and November 24, 2010.

[4] Although not specifically proposed by the permittee, "highly reactive materials" may be defined by Potential Acidity and any appropriate field or lab test agreeable to the permittee, the Corps and the EPA.

- Low-reactive durable rock wrapped in filter fabric to prevent clogging will be used for construction of the underdrain. Identification of low-reactive rock will be based on low Potential Acidity values[5].
- Diversions will be constructed around the fills so that surface runoff from upland areas will be intercepted and not infiltrate the fill. Diversion channels will be constructed to pass flows as dictated by the SMCRA regulations.
- The material placed at the top of the fill will be compacted as it is place to form an earthen cap reducing the void space between the particles and the associated potential for infiltration of water.
- The fills will be vegetated during construction after being brought to final grade to reduce erosion of the material.

Sediment Control BMPs
- Temporary sediment control structures such as silt fence, straw bales, rock checks, dikes, and/or channel barriers will be used, as necessary, to prevent the transport of sediment downstream.
- Sediment and erosion control measures will be inspected by a qualified individual appointed by the applicant's management at least twice per month and after every rainfall exceeding 0.5 inches in a 24 hour period (as measured at the project site) to ensure the structure and measures are functioning properly and to identify any required maintenance.
- Chemical treatment of the ponds will be used, if necessary and practicable to facilitate compliance with the projects KPDES permit.

In addition to the BMPs listed above, proposed by the applicant in supplemental information received by EPA on November 4 and November 24, 2010, EPA recommends that other BMPs should be implemented immediately in order to reduce the likelihood that water quality problems will occur. Such BMPs could include:
- taking further steps to minimize water infiltration into fill material using synthetic caps or liners;
- promoting diffuse discharges to mimic forested watersheds using techniques such as weep berm-forest passive treatment systems; and
- utilizing the Forest Reclamation Approach (FRA).

EPA recognizes that most, if not all, of these BMPs would be considered experimental practices under KDNR SMCRA regulations. EPA would strongly support efforts by the applicant to obtain authorization as needed from the KNDR and the Office of Surface Mining Reclamation and Enforcement to use these techniques.

C.   The permittee shall submit documentation to the Corps and EPA indicating all BMPs employed to minimize TDS and SC during the placement of fill material into waters of the United States and before and during mining and reclamation activities, including the construction of the backstacks and valley fills. The initial documentation must be submitted within 30 days of site preparation and commencement of construction of the rock underdrain. After this initial submittal, the permittee shall submit documentation

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[5] Although not specifically proposed by the permittee, "low-reactive durable rock" may also be defined as the most weathered upper strata and by any appropriate field or lab test agreeable to the permittee, the Corps and the EPA.

every 6 months unless the AMP has been triggered through Special Condition I.E or I.F., below. All monitoring data and analyses (effluent monitoring, in-stream chemical and biological monitoring, mitigation monitoring, and AMP trigger analysis) shall be reported to the Corps and EPA within 30 days of being collected.

D.   Prior to beginning discharge of materials into waters of the United States, the permittee shall reassess the need for excess spoil storage in valley fills, based on changes in fill construction described in Special Permit Condition I.B., above, to determine whether it is possible to avoid at least one fill, and submit documentation of that assessment to the Corps and EPA.

Before any material is discharged into waters of the United States for each subsequent pair of valley fills (see Special Permit Condition I.G., below), the applicant shall reassess the need for additional excess spoil storage in valley fills through an appropriate engineering analysis that includes comparison of actual mined coal tonnage, spoil generation rates, and the amount of spoil stored in valley fills with those permitted.

If the applicant (permittee) is successful in optimizing fill placement such that one or more valley fills is not necessary, or if the Corps or EPA determines that the permittee's analysis is insufficient or not compelling, the permitee shall protect any unfilled valleys by a permanent conservation easement to ensure that the stream continues to provide clean dilution water to the watershed.

E.   The permittee shall monitor the effluent of each sediment pond for conductivity two times per month and submit monthly flow-weighted conductivity, $\overline{K}$, following the commencement of discharges of material into waters of the United States to the Corps and EPA. The applicant must submit these data monthly to the agencies described below and must begin data collection and submittal immediately upon permit issuance and continue until final bond release. Monthly flow-weighted conductivity shall be calculated as follows:

$$\overline{K} = \frac{\sum_i (Q_i \times K_i)}{\sum_i Q_i}$$

where:
$\overline{K}$ = monthly flow-weighted conductivity, μS/cm
Q_i = flow for the ith sample, cfs
K_i = conductivity for the ith sample, μS/cm.

The monthly flow-weighted conductivity, $\overline{K}$, will be plotted as a time series and the trend in effluent conductivity calculated by linear regression, based on the most recent six month's data, beginning after completion of Initial Fill Construction[6]. The trend shall be

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[6] "Initial Fill Construction" is defined as "the stage of the hollow fill construction at which overburden material is placed in the hollow fill to the elevation of the base mining coal seam in that area" (Supplemental Material received November 4, 2010). It is noted that according to the MRP, this elevation is at or about 1,390 feet, the elevation of the Hazard 5a seam.

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calculated based on three month's data after completion of Initial Fill Construction until more data are available. If the trend indicates that any pond's monthly flow-weighted conductivity will exceed 500 µS/cm within the next three months, or if any two consecutive monthly flow-weighted conductivity values for any pond exceeds 500 µS/cm, then the permittee will conduct an analysis of the sources of effluent conductivity and develop a Phase I Adaptive Management Plan (AMP) to reduce effluent conductivity (or specific conductance, SC, and total dissolved solids, TDS). Examples of design alternatives, best management practices (BMP), and treatment technologies to include in the Phase I Adaptive Management Plan may include, but are not limited to:

- o The use of flocculents designed specifically to reduce total suspended solids/TDS/SC (with appropriate approval from the Kentucky Division of Water, KDOW); and
- o Floating siphons to decant the cleanest water prior to discharge to receiving streams.

The conductivity trend analysis and Phase I Adaptive Management Plan shall be submitted to the Corps and EPA for approval within 30 days of determining that the trend will exceed 500 µS/cm within the next three months for any pond, or within 30 days of determining that two consecutive monthly flow-weighted conductivity values for any pond have exceeded 500 µS/cm. The plan shall be implemented within 45 days of written approval by the Corps and EPA. Implementation of the Phase I AMP will continue until three consecutive monthly flow-weighted conductivity values are below 500 µS/cm for all ponds, and until the trend does not indicate that monthly flow-weighted conductivity will again exceed 500 µS/cm.

If either the calculated trend or the actual data indicate that monthly flow-weighted conductivity values for any pond will exceed or have exceeded 500 µS/cm continually for six months after implementation of the Phase I AMP, the permittee will retain, within 30 days, a consultant mutually agreed upon by the permittee, the Corps and EPA. The consultant shall prepare within 90 days recommendations for additional actions to reduce effluent conductivity (a Phase II AMP). These recommendations shall be implemented within 45 day of written approval by the Corps and EPA. This requirement will reiterate every six months after implementation of the approved additional actions as long as the trend or monthly flow-weighted conductivity values exceed 500 µS/cm.

F.   Background monitoring (in-stream).

The permittee shall monitor in-stream conductivity two times per month in Stacy Branch, Sugar Creek, and Yellow Creek to establish a baseline conductivity level against which future project impacts will be evaluated. The applicant must submit these data monthly to the agencies described under Special Permit Condition I.E, above, and must begin data collection and submittal immediately upon permit issuance and continue until final bond release. The baseline conductivity level will be calculated from these data using a method mutually agreeable to the Corps and EPA.

For each stream, monthly average conductivity will be plotted as a time series and the trend in effluent conductivity calculated by linear regression, based on the most recent six month's data. If any two consecutive monthly average conductivity values for any stream exceed 500 µS/cm or baseline conductivity level, whichever is greater, or if the trend indicates that any stream's monthly average conductivity will exceed 500 µS/cm or baseline conductivity level, whichever is greater, within the next three months, then the permittee will conduct an analysis of the causes of elevated in-stream conductivity, including any other discharges in the watershed (such as from underground mines), and develop a Phase I Adaptive Management Plan for Streams (AMP) to reduce in-stream conductivity, similar to that described under Special Permit Condition I.E., above.

The conductivity trend analysis and Phase I Adaptive Management Plan for Streams shall be submitted to the Corps and EPA for approval within 30 days of determining that two consecutive monthly average conductivity values for any stream have exceeded 500 µS/cm or baseline conductivity level, whichever is greater, or within 30 days of determining that the trend will exceed 500 µS/cm or baseline conductivity level, whichever is greater, within the next three months for any stream. The plan shall be implemented within 45 days of written approval by the Corps and EPA. Implementation of the Phase I AMP for Streams will continue until three consecutive monthly average conductivity values are below 500 µS/cm for all streams, and until the trend does not indicate that monthly average conductivity will again exceed 500 µS/cm.

If either the calculated trend or the actual data indicate that monthly average conductivity values for any stream will exceed or have exceeded 500 µS/cm or baseline conductivity level, whichever is greater, continually for six months after implementation of the Phase I AMP for streams, the permittee will retain, within 30 days, a consultant mutually agreed upon by the permittee, the Corps and EPA. The consultant shall prepare within 90 days recommendations for additional actions to reduce in-stream conductivity and/or to reduce conductivity from or eliminate any discharges in the watershed(s) (a Phase II AMP for Streams). These recommendations shall be implemented within 45 day of written approval by the Corps and EPA. This requirement will reiterate every six months after implementation of the approved additional actions as long as the trend or monthly average stream conductivity values exceed 500 µS/cm or baseline conductivity level, whichever is greater.

G.   Sequenced Fill Construction.

1) You are authorized to proceed with the construction of two valley fills: one of the larger fills (3, 4 or 6) and one of the smaller fills (2, 5 and 7) and their associated Sediment Ponds. You are further authorized to proceed with the construction of two more valley fills, one of the remaining larger fills and one of the remaining smaller fills, and their associated Sediment Ponds if and only if:

a) the monthly flow-weighted pond effluent conductivity values shall not exceed 500 µS/cm for any pond for two or more months consecutively since completion of Initial Fill Construction; and

b) the trend in pond effluent conductivity calculated as described above (based on the most recent six month's data collected after completion of Initial Fill Construction) indicates that monthly flow-weighted conductivity will not exceed 500 μS/cm for all ponds; and

c) the monthly average in-stream conductivity values shall not exceed 500 μS/cm or baseline conductivity level (as defined under Special Permit Condition I.F., above), whichever is higher, for any stream for two or more months consecutively for any stream; and

d) the trend in stream conductivity calculated as described above (based on the most recent six month's data) indicates that monthly average conductivity will not exceed 500 μS/cm or baseline conductivity level (as defined under Special Permit Condition I.F., above), whichever is higher, for all streams.

H.   Prior to any site disturbance the permitee shall reevaluate stream conditions on site using the Eastern Kentucky Stream Assessment Protocol and provide full documentation to the Corps and EPA. Based on the site evaluation, the applicant shall also provide the agencies with an updated Compensatory Mitigation Plan (CMP). Upon written approval of the agencies the applicant can proceed with discharges to waters of the United States in accordance with this permit and the approved CMP.

II.   Effluent and In-stream Chemical and Biological Monitoring

A. Effluent Monitoring

1. Parameters and Test Methods

a) Hydrologic permanence of outflow from the ponds should be monitored and recorded by a continuously recording measurement device.

b) The permittee should perform effluent monitoring of the parameters listed in Table 1, analyzed using EPA Test Methods in 40 CFR Part 136 by an licensed laboratory.[7]

c) When conducting effluent monitoring, the permittee must follow the appropriate and approved Kentucky Division of Water (KDOW) protocols, standard operating procedures, and quality assurance requirements as specified in the "Quality Assurance Project Plan (QAPP) for Individual Coal Mining Permits: Focus Monitoring for Water Quality, Biological Communities and Habitat Conditions."

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[7] Where EPA has approved more than one analytical method for a pollutant, the Agency expects that applicants and permittees would select methods that are able to quantify the presence of pollutants in a given discharge at concentrations that are low enough to determine compliance with Water Quality Criteria. Permit applicants should not use a less sensitive or less appropriate method, thus masking the presence of a pollutant in the discharge, when an EPA-approved method is available that can quantify the pollutant concentration at the lower levels needed for permit decision making. For purposes of permit applications and compliance monitoring, a method is "sufficiently sensitive" when (1) the method's quantitation level is at or below the level of the applicable water quality criterion for the pollutant or (2) the method's quantitation level is above the applicable water quality criterion, but the amount of pollutant in a facility's discharge is high enough that the method detects and quantifies the level of pollutant in the discharge.

The QAPP shall be submitted to the Corps, USEPA R4 and KDOW within 30 days of permit issuance. The Corps will coordinate approval of the QAPP with the agencies. The effluent monitoring may be included as part of the QAPP that has been or will be developed for the KPDES required monitoring, or it may be included in a separate QAPP. Receiving KDOW approval is not a requirement of the effluent monitoring Special Condition. The protocols are available on KDOW's website at: http://water.ky.gov/permitting/Pages/Mining.aspx

2. Sample Type
Grab samples shall be taken. Grab sample is defined as an individual sample of at least 100 milliliters collected at a randomly selected time over a period not exceeding fifteen minutes.

3. Sampling Frequency
The sampling frequency is as noted in Table 1. Effluent monitoring shall continue through final bond release. Samples that are required quarterly should be collected at least five (5) days apart, and the amount of precipitation for the previous 24 hour period should be recorded on-site and reported (to the nearest 0.1 inch) as part of the sampling report.

In the event that in-stream monitoring results show in-stream specific conductivity levels above 500 µS/cm, the permittee is required to increase the effluent monitoring frequency for all parameters to two times per month. Samples that are required twice per month should be collected at least five (5) days apart, and the amount of precipitation for the previous 48 hour period should be recorded on-site and reported (to the nearest 0.1 inch) as part of the sampling report.

4. Sampling Locations
The permittee should perform effluent monitoring from at least one outfall (i.e., a "representative outfall") in each receiving water body, to be specified in the NPDES permit by KDOW. Selected outfalls for each receiving water body should be representative of the effluent being discharged from the mine site and expected by KDOW to have the greatest impact on downstream water quality (e.g., the mine site area which is currently undergoing the most mining disturbance, or the outfall with the largest discharge) based on the information submitted in the permit application.

5. Reporting
Reports shall contain tabulated data (including sample station identification, date, and time) and graphs necessary to present information clearly and concisely, including all such tables and graphs necessary to summarize and present the entire period of record for each parameter and sample station. Latitude and longitude coordinates of all water quality monitoring locations with the applicable datum identified must be provided along with photographs and figures illustrating all sample locations. Calibration records of all *in-situ* multi-probe or single-probe water quality instruments and laboratory reports showing the analytical results must also be submitted.

All results should be clearly labeled with the applicable CWA permit number and KDNR DMP number and submitted to KDOW, the Corps, and EPA Region 4.

Results should be sent to EPA at: EPA Region 4 Water Protection Division
                                         Wetlands, Coastal & Oceans Branch, Mining Section
                                         61 Forsyth Street SW
                                         Atlanta, GA 30303-8960

Table 1 - Supplemental effluent and in-stream water quality monitoring parameters.

Parameter	Units	Method	Sample Frequency [1]
Bicarbonate Alkalinity	mg/l		Quarterly
Chlorides	mg/l	EPA 300.0	Quarterly
Discharge	Cfs	DOWSOP03019*	Quarterly
Dissolved oxygen	mg/l	DOWSOP03014*	Quarterly
Duration of discharge [2]	days		Continuous
Hardness (as $CaCO_3$)	mg/l	SM 2340B	Quarterly
pH	s.u.	DOWSOP03014*	Quarterly
Precipitation	inches		Continuous
Sulfates	mg/l	EPA 300.0	Quarterly
Specific conductance	µS/cm	EPA 120.1	Quarterly
Temperature	Deg C	DOWSOP03014*	Quarterly
Turbidity	Ntu	DOWSOP03014*	Quarterly
Total Dissolved Solids (TDS)	mg/l	SM 2540C	Quarterly
Total Calcium	µg/l	EPA 200.7	Quarterly
Total Magnesium	µg/l	EPA 200.7	Quarterly
Total Potassium	µg/l		Quarterly
Total Sodium	µg/l		Quarterly
Total Recoverable Antimony	µg/l	EPA 200.8	Quarterly
Total Recoverable Arsenic	µg/l	EPA 200.8	Quarterly
Total Recoverable Beryllium	µg/l	EPA 200.8	Quarterly
Total Recoverable Cadmium	µg/l	EPA 200.8	Quarterly
Total Recoverable Chromium (III)	µg/l		Quarterly
Total Recoverable Chromium (IV)	µg/l		Quarterly
Total Recoverable Copper	µg/l	EPA 200.8	Quarterly
Total Recoverable Iron	µg/l	EPA 200.8	Quarterly
Total Recoverable Lead	µg/l	EPA 200.8	Quarterly
Total Recoverable Manganese	µg/l	EPA 200.8	Quarterly
Total Recoverable Mercury	µg/l	EPA 1631E or 245.7	Quarterly
Total Recoverable Nickel	µg/l	EPA 200.8	Quarterly
Total Recoverable Selenium	µg/l	EPA 200.8	Quarterly
Total Recoverable Silver	µg/l	EPA 200.8	Quarterly
Total Recoverable Thallium	µg/l	EPA 200.8	Quarterly
Total Recoverable Zinc	µg/l	EPA 200.8	Quarterly

[1] The sample frequency increases to twice per month should the in-stream specific conductivity exceed 500 µS/cm.
[2] Duration of discharge from pond should be measured using a continuously recording data logger.
* KDOW, 2009. *In situ* Water Quality Measurements and Meter Calibration Standard Operating Procedure. Kentucky Department for Environmental Protection, Division of Water, Frankfort, Kentucky.

B.   Whole Effluent Toxicity (WET) Monitoring

Depending on the duration of the discharge, coal mining permits should require the permittee to perform acute and/or chronic WET tests on the representative outfalls (as specified above under "Effluent Monitoring") for all coal mining discharges. WET monitoring shall be

conducted quarterly. All results should be clearly labeled with the applicable CWA permit number and KDNR DMP number and submitted to KDOW, the Corps, and EPA Region 4.

In cases where monitoring data indicate a sedimentation pond with any volume of discharge lasting more than 4 consecutive days, chronic WET tests should be performed using *Ceriodaphnia dubia* and *Pimephales promelas* and using a dilution series that includes 100% effluent and the in-stream waste concentration. The end points should be reported as the inhibition concentration that affects 25% of the test organisms compared to the control (IC_{25}). Sampling should be performed quarterly. The operator should use WET testing procedures outlined in EPA's document entitled, "Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms" (October 2002).

In cases where the effluent discharge may be short in duration, it may be necessary to collect a high volume effluent sample and properly preserve it for use in the static-renewal test. Please refer to Section 8.5.4 on page 32 of EPA's document entitled, "Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms" (October 2002). Alternative acute WET test organisms are either *Daphnia magna* or *D. pulex* and *Pimaphales promelas*.

When conducting WET testing, the permittee must follow the appropriate and approved KDOW protocols, standard operating procedures, and quality assurance requirements as specified in the "Quality Assurance Project Plan (QAPP) for Individual Coal Mining Permits: Focus Monitoring for Water Quality, Biological Communities and Habitat Conditions." The QAPP shall be submitted to the Corps, USEPA R4 and KDOW within 30 days of permit issuance. The Corps will coordinate approval of the QAPP with the agencies. WET testing may be included as part of the QAPP that has been or will be developed for the KPDES required monitoring, or it may be included in a separate QAPP. Receiving KDOW approval is not a requirement of WET monitoring Special Condition. The protocols are available on KDOW's website at: http://water.ky.gov/permitting/Pages/Mining.aspx

C.   In-stream Chemical Monitoring

1. Parameters and Test Methods
The permittee should perform in-stream chemical monitoring of the parameters listed in Table 1, and analyzed using EPA Test Methods in 40 CFR Part 136 by an approved licensed laboratory.[1]

When conducting in-stream chemical monitoring, the permittee must follow the appropriate and approved KDOW protocols, standard operating procedures, and quality assurance requirements as specified in the QAPP. The QAPP shall be submitted to the Corps, USEPA R4 and KDOW within 30 days of permit issuance. The Corps will coordinate approval of the QAPP with the agencies. The in-stream chemical monitoring may be included as part of the QAPP that has been or will be developed for the KPDES required monitoring, or it may be included in a separate QAPP. Receiving KDOW approval is not a requirement of the in-stream chemical monitoring Special Condition. The protocols are available on KDOW's website at: http://water.ky.gov/permitting/Pages/Mining.aspx

2. Sample Type
Grab samples shall be taken. Grab sample is defined as an individual sample of at least 100 milliliters collected at a randomly selected time over a period not exceeding fifteen minutes.

3. Sample Frequency
The sampling frequency is as noted in Table 1. In-stream chemical monitoring shall continue through final bond release. Samples that are required quarterly should be collected at least five (5) days apart, and the amount of precipitation for the previous 24 hour period should be recorded on-site and reported (to the nearest 0.1 inch) as part of the sampling report.

In the event that in-stream monitoring results show in-stream specific conductivity levels above 500 µS/cm, the permittee is required to increase the in-stream chemical monitoring frequency for all parameters to two times per month. Samples that are required twice per month should be collected at least five (5) days apart, and the amount of precipitation for the previous 48 hour period should be recorded on-site and reported (to the nearest 0.1 inch) as part of the sampling report.

4. Sampling Locations
Samples should be taken from the following locations:

a. One sampling point located upstream of the sediment pond for each representative outfall, as specified above under "Effluent Monitoring." If there is no upstream location, an appropriate background location within the 12-digit hydrologic unit code should be used.

b. One in-stream monitoring site located immediately below the toe of the sediment pond for each representative outfall, as specified above under "Effluent Monitoring."

c. One sampling point located *the further* of 200 meters (656 feet) downstream of for each representative outfall, as specified above under "Effluent Monitoring," or the furthest downstream location that is upstream of any intervening tributaries. The sampling point should be downstream of riprap and other disturbance and located within a relatively natural and intact riparian zone.

d. One sampling point located downstream of the first intervening tributary.

5. Reporting
Reports shall contain tabulated data (including sample station identification, date, and time) and graphs necessary to present information clearly and concisely, including all such tables and graphs necessary to summarize and present the entire period of record for each parameter and sample station. Latitude and longitude coordinates of all water quality monitoring locations with the applicable datum identified must be provided along with photographs and figures illustrating all sample locations. Calibration records of all *in-situ* multi-probe or single-probe water quality instruments and laboratory reports showing the analytical results must also be submitted.

All results should be clearly labeled with the applicable CWA permit number and KDNR DMP number and submitted to KDOW, the Corps, and EPA Region 4.

D.   In-stream Biological Monitoring

The permittee should implement an annual biological assessment during critical low-flow conditions using approved state protocols.

1. Concurrent in-stream monitoring
In-stream samples for SC, TDS, pH, temperature, and dissolved oxygen should be taken at the same locations as the benthic samples.

2. Methods
Sampling should be avoided during periods of excessive precipitation and scouring floods. In cases where a large flow rate of the receiving water does not lend itself to a benthic assessment (i.e., only has non-wadeable streams), the permittee should perform a bioassessment using fish. Both fish and benthic macroinvertebrate studies should be performed for receiving water bodies that are conducive to fish assessments. Results from sampling either of the two assemblages may be used to determine if the water body is impaired.

When conducting in-stream biological monitoring, the permittee must follow the appropriate and approved KDOW protocols, standard operating procedures, and quality assurance requirements as specified in the QAPP. The QAPP shall be submitted to the Corps, USEPA R4 and KDOW within 30 days of permit issuance. The Corps will coordinate approval of the QAPP with the agencies. The in-stream biological monitoring may be included as part of the QAPP that has been or will be developed for the KPDES required monitoring, or it may be included in a separate QAPP. Receiving KDOW approval is not a requirement of the in-stream biological monitoring Special Condition. The protocols are available on KDOW's website at: http://water.ky.gov/permitting/Pages/Mining.aspx

3. Sampling Frequency
Sampling times will occur consistent with accepted Kentucky protocols (i.e. sample index periods). Sampling will occur annually through final bond release. Sampling should be avoided during periods of excessive precipitation and scouring floods. In cases where a large flow rate of the receiving water does not lend itself to a benthic assessment (i.e., non-wadeable streams), the permittee should perform a bioassessment using fish. Both fish and benthic macroinvertebrate studies should be performed for receiving water bodies that are conducive to fish assessments. Results from sampling either of the two assemblages may be used to determine if the water body is impaired.

4. Sampling Locations
Use the same locations as shown above for in-stream chemical monitoring.

5. Reporting
Reports shall contain tabulated data (including sample station I.D., date, and time) and graphs necessary to present information clearly and concisely, including all tables, indices of biotic integrity, and graphs necessary to summarize and present the entire period of record for each parameter and sample station. Latitude and longitude coordinates of all water quality monitoring locations with the applicable datum identified must be provided along with photographs and figures illustrating all sample locations. Calibration records of all *in-situ*

multi-probe or single-probe water quality instruments and laboratory reports showing the analytical results must also be submitted.

All results should be clearly labeled with the applicable CWA permit number and KDNR DMP number and submitted to KDOW, the Corps, and EPA Region 4.

Enclosure 2
Adaptive Management Plan Implementation Timeline—Pond Effluent

Phase	Action	Time allowed	Estimated time since initial discharge of fill material into waters of the U.S.[8]
Pre-AMP	Initial Fill Construction[9]	Not specified in Special Condition; estimate 3 months	Not specified in Special Condition; estimate 3 months
	Monitoring after Initial Fill Construction	2 months minimum[10]	5 months
AMP Phase I (if applicable)	Submit AMP I	30 days after AMP I trigger	6 months
	Approve AMP I	Not specified in Special Condition; estimate 45 days	7.5 months
	Implement AMP I	45 days after AMP I Approval	9 months
	Monitor AMP I	6 months minimum	15 months
AMP Phase II (if applicable)	Retain consultant	30 days after AMP II trigger	16 months
	Develop and submit AMP II	90 days after AMP II trigger	19 months
	Approve AMP II	Not specified in Special Condition, estimate 45 days	20.5 months
	Implement AMP II	45 days after AMP II approval	22 months
	Monitor AMP II	6 months minimum	28 months
Additional Iterations (if applicable)	Develop and submit AMP	90 days after AMP trigger	31 months
	Approve AMP	Not specified in Special Condition, estimate 45 days	32.5 months
	Implement AMP	45 days after AMP approval	34 months
	Monitor AMP	6 months minimum	40 months

[8] Estimates assume minimum times allowed.

[9] "Initial Fill Construction" is defined as "the stage of the hollow fill construction at which overburden material is placed in the hollow fill to the elevation of the base mining coal seam in that area" (Supplemental Material received November 4, 2010). It is noted that according to the MRP, this elevation is at or about 1,390 feet, the elevation of the Hazard 5a seam. Note that monitoring data shall be collected and submitted immediately upon permit issuance and until final bond release.

[10] Monitoring in any Phase will continue until the next Phase is triggered or permit expiration, whichever occurs first.

Adaptive Management Plan Implementation Timeline—In-stream

Phase	Action	Time allowed	Estimated time since permit issuance[11]
Pre-AMP	Background monitoring	2 months minimum[12]	2 months
AMP Phase I (if applicable)	Submit AMP I	30 days after AMP I trigger	3 months
	Approve AMP I	Not specified in Special Condition; estimate 45 days	4.5 months
	Implement AMP I	45 days after AMP I Approval	6 months
	Monitor AMP I	6 months minimum	12 months
AMP Phase II (if applicable)	Retain consultant	30 days after AMP II trigger	13 months
	Develop and submit AMP II	90 days after AMP II trigger	16 months
	Approve AMP II	Not specified in Special Condition, estimate 45 days	17.5 months
	Implement AMP II	45 days after AMP II approval	19 months
	Monitor AMP II	6 months minimum	25 months
Additional Iterations (if applicable)	Develop and submit AMP	90 days after AMP trigger	28 months
	Approve AMP	Not specified in Special Condition, estimate 45 days	29.5 months
	Implement AMP	45 days after AMP approval	31 months
	Monitor AMP	6 months minimum	3 months

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[11] Estimates assume minimum times allowed.

[12] Monitoring in any Phase will continue until the next Phase is triggered or permit expiration, whichever occurs first.

Colonel Robert D. Peterson
District Engineer
Huntington District
U.S. Army Corps of Engineers
502 Eighth Street
Huntington, West Virginia 25701

JUN 2 1 2010

Dear Colonel Peterson:

    The U.S. Environmental Protection Agency (EPA) has been participating in discussions with your staff and with representatives of Coal-Mac Inc. (applicant) to seek resolution of concerns expressed by EPA regarding the proposed Pine Creek Surface Mine. Pine Creek Surface Mine is one of the remaining sixteen projects located in West Virginia and identified for the enhanced coordination procedures (ECP) established in the Memorandum of Understanding (MOU) signed by our respective agencies and the Department of Interior on June 11, 2009. The 60-day ECP timeframe for resolution of issues surrounding this project began on April 6, 2010 and expired on June 4, 2010. EPA sent a letter requesting a 15 day extension for review of the project; that extension expires on June 19, 2010.

    On April 1, 2010, EPA released interim final guidance to the Regional offices titled: *Guidance on Improving EPA Review of Appalachian Surface Coal Mining Operations under the Clean Water Act, National Environmental Policy Act, and the Environmental Justice Executive Order* (SCM Guidance). The SCM Guidance clarifies EPA's regulations as they apply to discharges associated with surface coal mining practices and provides a framework for the Regions when they review permits for discharges associated with Appalachian surface mining projects. EPA Region III utilized the regulations and this Guidance during its review of the Coal Mac proposal. EPA recently also released two Office of Research and Development (ORD) reports: *The Effects of Mountaintop Mines and Valley Fills on Aquatic Ecosystems of the Central Appalachian Coalfields,* and *A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams (Benchmark Conductivity Study).* The ORD reports are being submitted to the EPA Science Advisory Board (SAB) for review and are also publicly available. In the interim, EPA views the reports as providing information, along with published, peer-reviewed scientific literature, that may inform permit reviews.

    During the project review process as provided by the June 11, 2009 Memorandum to the Field, EPA identified four areas of general concern. These included avoidance and minimization, water quality impacts, cumulative effects, and mitigation. The project as proposed by Coal-Mac Inc. will impact 14,530 linear feet of stream channel and disturb 759 surface acres. The streams on-site are good quality and are providing clean, freshwater dilution to the Left Fork of Pine Creek. We commend Coal-Mac for its efforts to address EPA's concerns based on our

regulations and clarified by the SCM Guidance. EPA believes that a permit decision may move forward consistent with the application as modified by this letter.

Avoidance and Minimization

The applicant performed a comprehensive alternatives analysis as part of the original application. Through the applicant's upfront efforts impacts to 22% of the stream resources within the project area were avoided. The applicant proposes to haul approximately 4.1 million tons of material to the adjacent mine (Pheonix No. 4 Surface Mine). The applicant proposes to raise the deck of the valley fills 100 feet beyond that which is required by the West Virginia Approximate Original Contour/Fill Optimization process. Where practicable the applicant has maximized the amount of spoil returned to the mine bench and minimized the amount of excess spoil that must be disposed of in streams. Following the initiation of the ECP process, the applicant evaluated alternatives in valley fill construction and has incorporated best management practices that are expected to reduce the likelihood of increased loading of total dissolved solids (TDS) and specific conductivity levels to minimize water quality impacts and protect against significant degradation of downstream aquatic resources. These include a materials handling plan to minimize exposure of mineral-rich overburden to surface waters and groundwater, and modification of fill construction to maximize surface water runoff and minimize infiltration of water through the fill.

In addition, the applicant has modified the mine plan in an effort to minimize the amount of land disturbed at any one point in time during the operation. The original plan proposed to have the full mine area disturbed and all three valley fills active within 12-18 months of commencing operation. The revised mine plan proposes the concurrent use of Valley Fills 1 and 3 within approximately 6 months, but represents a reduction of surface acres of disturbance at any point in time during operation by up to 25% within one year of operation. The applicant's proposal would delay the use of Valley Fill 2 until approximately 3 years from the beginning of the operation. While the applicant's efforts in this regard are appreciated, the proposal essentially calls for concurrent construction of Valley Fills 1 and 3. As set forth in more detail below, EPA recommends that the three valley fills be constructed sequentially, with earlier valley fills fully constructed and monitored prior to initial construction of subsequent fills to ensure that predicted water quality outcomes are achieved.

Water Quality and Significant Degradation

To address the Agency's water quality concerns, the applicant has proposed to incorporate Best Management Practices recommended in the April 1 SCM Guidance. Based on peer-reviewed studies examining the relationship between conductivity and water quality impairment in Appalachia, EPA anticipates that projects with predicted conductivity levels below 300 µS/cm generally will not cause a water quality standard violation or significant degradation of the aquatic ecosystem. However, EPA expects that in-stream conductivity levels above 500 µS/cm are likely to be associated with adverse impacts that could rise to a level of significant degradation of the aquatic ecosystem. EPA has not been provided any information regarding site-specific conditions that differ from those studies. The Corps, EPA and the applicant have worked to develop protective permit conditions to ensure in-stream specific conductivity remains at levels that will not cause or contribute to degradation to water quality, including setting threshold limits within the permit of 300 µS/cm and 500 µS/cm, sequential construction of the

valley fills as described in the SCM Guidance document; a demonstration that specific conductivity at the monitoring locations remains on average below 500 µS/cm before the commencement of the next valley fill may begin.

To support this demonstration, a supplemental enhanced monitoring plan has been included with the project proposal as described in the applicant's Supplemental Monitoring and Adaptive Management Plan document. The applicant has agreed to monitor for physical, biological, and chemical parameters. The chemical parameters that will be monitored include, but are not limited to flow, pH, iron, manganese, aluminum, selenium, TDS, total suspended solids (TSS), sulfates, chlorides and specific conductivity.

The applicant proposes two conductivity thresholds for adaptive management. The first is at 300 µS/cm. If the linear trend in the twice-monthly monitoring data indicates an exceedance of 300 µS/cm below Valley Fill 1 and/or Valley Fill 3, the applicant will implement an adaptive management plan (AMP) to address the trend. The second threshold is at 500 µS/cm. The applicant proposes that, if a linear trend in twice-monthly monitoring indicates an exceedance of 500 µS/cm below Valley Fill 1, the applicant will provide additional mitigation focused on chemical improvements in the watershed. With respect to construction of Valley Fills 1 and 3, the applicant proposes to commence construction of Valley Fill 1 and to demonstrate that the average conductivity values downstream of Valley Fill 1 remain below 500 µS/cm within six months from construction of Pond 1 or after the construction of the first three lifts within Valley Fill 1, which ever period of time is longer. The applicant proposes that, if the foregoing condition is achieved, the applicant be authorized to proceed with construction of Valley Fill 3. If the foregoing condition is not achieved, the applicant proposes that it would not be authorized to proceed with construction of Valley Fill 3 until and unless successful remediation occurs. With respect to construction of Valley Fill 2, the applicant proposes to monitor both Valley Fills 1 and 3 during construction and demonstrate that average conductivity values downstream of both fills have remained below 500 µS/cm. If this condition is achieved, construction of Valley Fill 2 may proceed. Under this scenario, the applicant anticipates a period of three years between construction of Pond 1 and commencement of construction of Valley Fill 2. The applicant would not be allowed to proceed to Valley Fill 2 until and unless successful remediation occurs.

While the applicant's proposal attempts to address the Agency SCM Guidance, EPA remains concerned that the proposal essentially calls for concurrent construction of Valley Fills 1 and 3. The applicant has not demonstrated that the anticipated approximate 6 month period between construction of Pond 1 and commencement of construction at Valley Fill 3 is a sufficient monitoring period to meaningfully evaluate impacts from Valley Fill 1. For that reason, EPA recommends that each proposed valley fill be constructed to its completion and monitored over a period of time to evaluate whether significant degradation is occurring. This would allow for a comprehensive demonstration that Valley Fill 1 is consistent with the conductivity benchmark of 500 µS/cm included in the SCM Guidance and will not result in significant degradation in the receiving streams.Accordingly, EPA recommends that only Valley Fill 1 be authorized immediately using previously agreed-upon underdrain and landscape best management practices. Authorization of only Valley Fill 1 allows for time to assess the effects of removing the contribution of dilution waters with low conductivity to the Left Fork of Pine Creek where conductivity levels approach 500 µS/cm. The data from Valley Fill 1 should be utilized to determine whether to authorize remaining valley fills.

Mitigation

The applicant has proposed on-site stream restoration and creation of 40,000+ linear feet of stream (greater than 2:1 ratio). The plan includes a significant monitoring plan and benchmarks for success, an adaptive management plan that provides back up plans if the projects are unsuccessful and provides for upfront financial assurances. The applicant's benchmarks of success include biological, chemical and physical measures and are intended to replace the lost functions within the immediate watershed. The primary goal of these created stream channels is to become functioning stream channels that meet Clean Water Act requirements and meet the State's designated use for aquatic life. EPA believes the proposed mitigation is consistent with CWA regulations and the considerations provided in the April 1 SCM Guidance document.
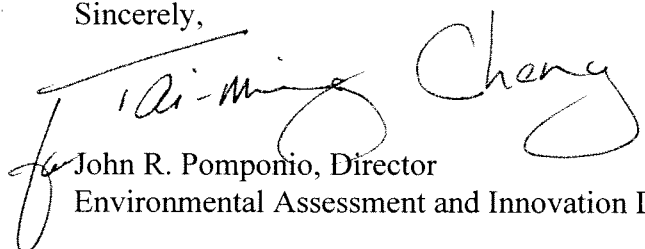
Cumulative Impacts

To address cumulative impacts, the applicant has offered to deed restrict three areas previously permitted to be filled on the Phoenix No. 5 Surface Mine operation. The Phoenix No. 5 operation was authorized to construct 5 valley fills. Two valley fills have been constructed. The applicant will deed restrict the three remaining unfilled sites. Those areas will therefore not be subject to filling now or in the future. This is an avoidance of impacts to 3,900 linear feet of stream channel and represents a 39.5% reduction of impacts within the Pine Creek watershed. The average conductivity values for these three streams are below 350 μS/cm and West Virginia Stream Condition Index scores greater than 85, indicating a very good biological community. In addition, the applicant has proposed to provide mitigation concurrently with the mining operation focused on improving the water quality through the reduction of TDS in the immediate watershed. There currently exists 4 deep mine discharges that are contributing to the loading of TDS on Left Fork of Pine Creek, and on Pine Creek, that the applicant is evaluating and is proposing to address.

EPA believes that a permit decision may move forward consistent with the application as modified by the Supplemental Monitoring and Adaptive Management Plan and as further modified by this letter. Incorporation of these modifications into enforceable conditions is recommended. EPA requests that we have the opportunity to review and comment on the draft permit and special conditions prior to finalization.

EPA appreciates the work your staff and Coal-Mac Inc. have undertaken to address the Agency's concerns. We look forward to continuing coordination as the permit is finalized. If you have any questions please don't hesitate to contact me or Jeff Lapp of my staff at 215-814-2717.

Sincerely,

John R. Pomponio, Director
Environmental Assessment and Innovation Division

Matthew Klasen/DC/USEPA/US	To	Denis Borum	
01/05/2011 11:13 AM	cc	Gregory Peck	
	bcc		
	Subject	Fw: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)	

Hey Denis,

(b) (5)

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229
----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/05/2011 11:06 AM -----

From:	Matthew Klasen/DC/USEPA/US
To:	Chris Thomas/R4/USEPA/US@EPA, Deborah Nagle/DC/USEPA/US@EPA, Denis Borum/DC/USEPA/US@EPA, Diane Jones-Coleman/DC/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Js Wilson/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Linda Boornazian/DC/USEPA/US@EPA, Marcus Zobrist/DC/USEPA/US@EPA, MichaelG Lee/DC/USEPA/US@EPA, Sharmin Syed/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Tom Laverty/DC/USEPA/US@EPA
Cc:	Bob Sussman/DC/USEPA/US@EPA, Nancy Stoner/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA
Date:	01/05/2011 11:03 AM
Subject:	Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Hi everyone,

As promised on yesterday morning's mining call, attached is an updated draft response letter to Congressman Rahall regarding EPA 402 actions in WV (not on Spruce). I've included both a clean version and a Track Changes version.

I've taken the original draft that Evelyn put together back in December, added the mid-December comments from Mark in R4, incorporated preliminary edits/comments from Mike Lee in OGC, and made some additional edits (like moving the specific question responses to the end of the letter rather than in the middle).

I'd be happy to continue to be the compiler of edits to this, or Evelyn or others in R3 could take that on.

Let me know what works best.

Comments by noon tomorrow I think would be great, in prep for sending this out either later this week or next week (probably the latter, given Spruce).

Thanks,
Matt   ATTACHMENTS REDACTED – DELIBERATIVE

2011-01-05 Draft Rahall Response on 402 - Track Changes.docx   2011-01-05 Draft Rahall Response on 402 - Clean.docx

----
Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Gregory Peck/DC/USEPA/US

01/05/2011 11:14 AM

To   Karyn Wendelowski

cc   Christopher Hunter, David Evans, Denise Keehner, Kevin Minoli, Matthew Klasen, Tanya Code, Betsaida Alcantara

bcc

Subject   Re: Feedback on press release

(b) (5)

                ATTACHMENT REDACTED - DELIBERATIVE

Mining Spruce DRAFT PR JAN 05 11.docx

Karyn Wendelowski	(b) (5)	01/05/2011 10:44:25 AM

From: Karyn Wendelowski/DC/USEPA/US
To: Gregory Peck/DC/USEPA/US@EPA
Cc: Christopher Hunter/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Tanya Code/DC/USEPA/US@EPA
Date: 01/05/2011 10:44 AM
Subject: Re: Feedback on press release

(b) (5)

Re: Feedback on press release

Re: Feedback on press release

Gregory Peck   to: Matthew Klasen   01/05/11 09:16 AM

Cc: Christopher Hunter, David Evans, Denise Keehner, Tanya Code, Karyn Wendelowski, Kevin Minoli

---

I would like to get folks reactions to the changes. (b) (5)

Matthew Klasen	Attached is a scan of Nancy's hard-copy edits to...	01/05/2011 09:12:45 AM

From: Matthew Klasen/DC/USEPA/US
To: Christopher Hunter/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA
Cc: Tanya Code/DC/USEPA/US@EPA
Date: 01/05/2011 09:12 AM
Subject: Re: Feedback on press release

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making edits, presumably in prep for sending a new version to OEA in advance of (or after) the briefing for Bob this afternoon.

Thanks,
Matt

[attachment "2010-01-05 Nancy edits to Spruce PR.pdf" deleted by Gregory Peck/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Christopher Hunter	Thanks Nancy, Matt or I will be by later today to...	01/05/2011 08:15:36 AM

From:	Christopher Hunter/DC/USEPA/US
To:	Nancy Stoner/DC/USEPA/US@EPA
Cc:	David Evans/DC/USEPA/US@EPA, "Denise Keehner" <keehner.denise@epa.gov>, Matthew Klasen/DC/USEPA/US@EPA
Date:	01/05/2011 08:15 AM
Subject:	Re: Feedback on press release

Thanks Nancy,
Matt or I will be by later today to pick up the edits. Also, we should have a revised draft of the executive summary for your review later today or tomorrow morning.

Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Nancy Stoner	My proposed line edits will be on Martha's desk...	01/05/2011 07:44:53 AM

From:	Nancy Stoner/DC/USEPA/US
To:	"Denise Keehner" <keehner.denise@epa.gov>, David Evans/DC/USEPA/US@EPA, "Christopher Hunter" <Hunter.Christopher@epamail.epa.gov>
Date:	01/05/2011 07:44 AM
Subject:	Feedback on press release

My proposed line edits will be on Martha's desk when I get in (by 9). Not difficult. Thx

Gregory Peck/DC/USEPA/US

01/05/2011 11:14 AM

To   Karyn Wendelowski

cc   Christopher Hunter, David Evans, Denise Keehner, Kevin Minoli, Matthew Klasen, Tanya Code, Betsaida Alcantara

bcc

Subject   Re: Feedback on press release

(b) (5)

ATTACHMENT REDACTED - DELIBERATIVE

Mining Spruce DRAFT PR JAN 05 11.docx

Karyn Wendelowski	(b) (5)	01/05/2011 10:44:25 AM

From: Karyn Wendelowski/DC/USEPA/US
To: Gregory Peck/DC/USEPA/US@EPA
Cc: Christopher Hunter/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Tanya Code/DC/USEPA/US@EPA
Date: 01/05/2011 10:44 AM
Subject: Re: Feedback on press release

(b) (5)

Re: Feedback on press release

Re: Feedback on press release 📄

Gregory Peck   to: Matthew Klasen   01/05/11 09:16 AM

Cc: Christopher Hunter, David Evans, Denise Keehner, Tanya Code, Karyn Wendelowski, Kevin Minoli

(b) (5)

Matthew Klasen	Attached is a scan of Nancy's hard-copy edits to...	01/05/2011 09:12:45 AM

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To: Christopher Hunter/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA
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Thanks,
Matt

[attachment "2010-01-05 Nancy edits to Spruce PR.pdf" deleted by Gregory Peck/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Christopher Hunter	Thanks Nancy, Matt or I will be by later today to...		01/05/2011 08:15:36 AM

From:	Christopher Hunter/DC/USEPA/US
To:	Nancy Stoner/DC/USEPA/US@EPA
Cc:	David Evans/DC/USEPA/US@EPA, "Denise Keehner" <keehner.denise@epa.gov>, Matthew Klasen/DC/USEPA/US@EPA
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Subject:	Re: Feedback on press release

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Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Nancy Stoner	My proposed line edits will be on Martha's desk...		01/05/2011 07:44:53 AM

From:	Nancy Stoner/DC/USEPA/US
To:	"Denise Keehner" <keehner.denise@epa.gov>, David Evans/DC/USEPA/US@EPA, "Christopher Hunter" <Hunter.Christopher@epamail.epa.gov>
Date:	01/05/2011 07:44 AM
Subject:	Feedback on press release

My proposed line edits will be on Martha's desk when I get in (by 9). Not difficult. Thx

Tom Laverty/DC/USEPA/US
01/05/2011 12:46 PM

To   Sharmin Syed, David Hair, Colleen Forestieri, Js Wilson

cc   Sarita Hoyt, Martha Segall, Marcus Zobrist

bcc

Subject   Fw: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Folks,

have you had a chance to review this?   Reactions?

thanks

Tom

----- Forwarded by Tom Laverty/DC/USEPA/US on 01/05/2011 12:45 PM -----

From:	Matthew Klasen/DC/USEPA/US
To:	Chris Thomas/R4/USEPA/US@EPA, Deborah Nagle/DC/USEPA/US@EPA, Denis Borum/DC/USEPA/US@EPA, Diane Jones-Coleman/DC/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Js Wilson/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Linda Boornazian/DC/USEPA/US@EPA, Marcus Zobrist/DC/USEPA/US@EPA, MichaelG Lee/DC/USEPA/US@EPA, Sharmin Syed/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Tom Laverty/DC/USEPA/US@EPA
Cc:	Bob Sussman/DC/USEPA/US@EPA, Nancy Stoner/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA
Date:	01/05/2011 11:03 AM
Subject:	Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Hi everyone,

As promised on yesterday morning's mining call, attached is an updated draft response letter to Congressman Rahall regarding EPA 402 actions in WV (not on Spruce). I've included both a clean version and a Track Changes version.

(b) (5)

Comments by noon tomorrow I think would be great, in prep for sending this out either later this week or next week (probably the latter, given Spruce).

Thanks,
Matt

ATTACHMENTS REDACTED – DELIBERATIVE

2011-01-05 Draft Rahall Response on 402 - Track Changes.docx   2011-01-05 Draft Rahall Response on 402 - Clean.docx

----

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Matthew
Klasen/DC/USEPA/US

01/05/2011 12:49 PM

To Kevin Minoli

cc Stefania Shamet, Christopher Hunter, Gregory Peck, Karyn
Wendelowski

bcc

Subject Your next batch: 243A-307A

Hey Kevin,

Here's your next set (33 pages in total): 243A-307A.

These responses are mostly mitigation, but there are a couple on alternatives and a couple at the end that raise "other considerations" and our overall conclusions.

Let me know if you have any questions. Stef sent along edits this morning on the remaining chunk, and I'll get back to those after the 1 pm discussion with Bob.

Thanks,
Matt

ATTACHMENT REDACTED – DELIBERATIVE

2011-01-05 243A-307A for Kevin.docx

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Kevin Minoli/DC/USEPA/US

01/05/2011 12:51 PM

To Gregory Peck

cc

bcc

Subject Fw: Feedback on press release

(b) (5) Attorney-Client Privilege

----- Forwarded by Kevin Minoli/DC/USEPA/US on 01/05/2011 12:49 PM -----

From:	Denise Keehner/DC/USEPA/US
To:	Gregory Peck/DC/USEPA/US@EPA
Cc:	Betsaida Alcantara/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Tanya Code/DC/USEPA/US@EPA
Date:	01/05/2011 11:31 AM
Subject:	Re: Feedback on press release

ATTACHMENT REDACTED – DELIBERATIVE

Mining Spruce DRAFT PR JAN 05 11dkedits.docx

Christopher Hunter/DC/USEPA/US

01/05/2011 01:39 PM

To   "Brian Frazer"

cc

bcc

Subject   Fw: Feedback on press release

Chris Hunter
US EPA, Wetlands Protection Division
(202) 566-1454 (t)
(202) 573-6478 (c)
   Matthew Klasen

  ----- Original Message -----
    From: Matthew Klasen
    Sent: 01/05/2011 09:12 AM EST
    To: Christopher Hunter; David Evans; Denise Keehner; Gregory Peck
    Cc: Tanya Code
    Subject: Re: Feedback on press release

Attached is a scan of Nancy's hard-copy edits to the Spruce release. I'll give the hard copy to Greg for making edits, presumably in prep for sending a new version to OEA in advance of (or after) the briefing for Bob this afternoon.

Thanks,
Matt

ATTACHMENT REDACTED – DELIBERATIVE

2010-01-05 Nancy edits to Spruce PR.pdf

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Christopher Hunter	Thanks Nancy, Matt or I will be by later today to...	01/05/2011 08:15:36 AM

From:	Christopher Hunter/DC/USEPA/US
To:	Nancy Stoner/DC/USEPA/US@EPA
Cc:	David Evans/DC/USEPA/US@EPA, "Denise Keehner" <keehner.denise@epa.gov>, Matthew Klasen/DC/USEPA/US@EPA
Date:	01/05/2011 08:15 AM
Subject:	Re: Feedback on press release

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Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454

hunter.christopher@epa.gov

| Nancy Stoner | My proposed line edits will be on Martha's desk... | 01/05/2011 07:44:53 AM |

From:	Nancy Stoner/DC/USEPA/US
To:	"Denise Keehner" <keehner.denise@epa.gov>, David Evans/DC/USEPA/US@EPA, "Christopher Hunter" <Hunter.Christopher@epamail.epa.gov>
Date:	01/05/2011 07:44 AM
Subject:	Feedback on press release

My proposed line edits will be on Martha's desk when I get in (by 9). Not difficult. Thx

Christopher
Hunter/DC/USEPA/US

01/05/2011 01:40 PM

To "Brian Frazer"

cc

bcc

Subject Fw: Feedback on press release

Chris Hunter
US EPA, Wetlands Protection Division
(202) 566-1454 (t)
(202) 573-6478 (c)
   Gregory Peck

----- Original Message -----
From: Gregory Peck
Sent: 01/05/2011 11:14 AM EST
To: Karyn Wendelowski
Cc: Christopher Hunter; David Evans; Denise Keehner; Kevin Minoli; Matthew
Klasen; Tanya Code; Betsaida Alcantara
Subject: Re: Feedback on press release

(b) (5)

ATTACHMENT REDACTED - DELIBERATIVE

Mining Spruce DRAFT PR JAN 05 11.docx

Karyn Wendelowski   (b) (5)   01/05/2011 10:44:25 AM

From:	Karyn Wendelowski/DC/USEPA/US
To:	Gregory Peck/DC/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Tanya Code/DC/USEPA/US@EPA
Date:	01/05/2011 10:44 AM
Subject:	Re: Feedback on press release

(b) (5)

Re: Feedback on press release

Re: Feedback on press release

Gregory Peck to: Matthew Klasen   01/05/11 09:16 AM

Cc: Christopher Hunter, David Evans, Denise Keehner, Tanya Code, Karyn
Wendelowski, Kevin Minoli

Maybe the question turns more on what we want our message to be?

| Matthew Klasen | Attached is a scan of Nancy's hard-copy edits to... | 01/05/2011 09:12:45 AM |

From: Matthew Klasen/DC/USEPA/US
To: Christopher Hunter/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA
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Thanks,
Matt

[attachment "2010-01-05 Nancy edits to Spruce PR.pdf" deleted by Gregory Peck/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

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From: Christopher Hunter/DC/USEPA/US
To: Nancy Stoner/DC/USEPA/US@EPA
Cc: David Evans/DC/USEPA/US@EPA, "Denise Keehner" <keehner.denise@epa.gov>, Matthew Klasen/DC/USEPA/US@EPA
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Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

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From: Nancy Stoner/DC/USEPA/US
To: "Denise Keehner" <keehner.denise@epa.gov>, David Evans/DC/USEPA/US@EPA, "Christopher Hunter" <Hunter.Christopher@epamail.epa.gov>
Date: 01/05/2011 07:44 AM
Subject: Feedback on press release

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**Matthew
Klasen/DC/USEPA/US**

01/05/2011 02:08 PM

To Gregory Peck

cc

bcc

Subject Press release and Q&As

Here's the Denise-edited release (both Track Changes and clean) as well as the doc with as much progress as I've made on the Q&As.

Thanks,
Matt

Mining Spruce DRAFT PR JAN 05 11 - TC.docx   Mining Spruce DRAFT PR JAN 05 11 - Clean.docx

2011-01-04a Draft Spruce Q&As.doc

ATTACHMENTS REDACTED – DELIBERATIVE

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

MichaelG Lee/DC/USEPA/US
01/05/2011 03:58 PM

To   Matthew Klasen

cc   Js Wilson

bcc

Subject   Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Matt,
Here are my quick edits/comments. Let me know if you find out that we've got substantially more time on this -- I may run it past some folk in my shop with more specialized knowledge on a topic or two.

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-05 Draft Rahall Response on 402 - Clean.doc

Mike

Michael G. Lee
Office of General Counsel
(202) 564-5486

Matthew Klasen	Mike, Stef, and Ev: (b) (5)	01/05/2011 11:44:30 AM

From:	Matthew Klasen/DC/USEPA/US
To:	MichaelG Lee/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA
Date:	01/05/2011 11:44 AM
Subject:	Re: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Mike, Stef, and Ev:

(b) (5)

Anyway, just a heads up. Mike and Ev, if you could take a look at this soon, that would be great. Stef, I know you have nothing else you're working on, but you may also have to look at this fairly quickly. We can ask Bob and folks at the 1:00.

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Matthew Klasen	Hi everyone, As promised on yesterday mornin...	01/05/2011 11:03:17 AM

From:	Matthew Klasen/DC/USEPA/US
To:	Chris Thomas/R4/USEPA/US@EPA, Deborah Nagle/DC/USEPA/US@EPA, Denis Borum/DC/USEPA/US@EPA, Diane Jones-Coleman/DC/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Js Wilson/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Linda

Hi everyone,

As promised on yesterday morning's mining call, attached is an updated draft response letter to Congressman Rahall regarding EPA 402 actions in WV (not on Spruce). I've included both a clean version and a Track Changes version.

I've taken the original draft that Evelyn put together back in December, added the mid-December comments from Mark in R4, incorporated preliminary edits/comments from Mike Lee in OGC, and made some additional edits (like moving the specific question responses to the end of the letter rather than in the middle).

I'd be happy to continue to be the compiler of edits to this, or Evelyn or others in R3 could take that on. Let me know what works best.

Comments by noon tomorrow I think would be great, in prep for sending this out either later this week or next week (probably the latter, given Spruce).

Thanks,
Matt

[attachment "2011-01-05 Draft Rahall Response on 402 - Track Changes.docx" deleted by Matthew Klasen/DC/USEPA/US] [attachment "2011-01-05 Draft Rahall Response on 402 - Clean.docx" deleted by Matthew Klasen/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Stefania Shamet/R3/USEPA/US

01/05/2011 04:00 PM

To   Matthew Klasen

cc

bcc

Subject   114-240

(b) (5)

He's going to revise those tonight and will send in the am.

ATTACHMENT REDACTED – DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responsessds.docx

Christopher Hunter/DC/USEPA/US

01/05/2011 04:11 PM

To "Kevin Minoli", "Palmer Hough"

cc

bcc

Subject Fw: Feedback on press release

In case you'd like to follow along.
Chris Hunter
US EPA, Wetlands Protection Division
(202) 566-1454 (t)
(202) 573-6478 (c)
   Christopher Hunter

----- Original Message -----
   From: Christopher Hunter
   Sent: 01/05/2011 08:45 AM EST
   To: Matthew Klasen
   Subject: Re: Feedback on press release

I'm going to be in a lot of meetings today, so I thought I would get this done early. We'll see if Tanya has any response, but feel free to combine this doc with yours.

Chris

ATTACHMENT REDACTED - DELIBERATIVE

Comments and Responses for Denise.docx

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Matthew Klasen	Ok -- I put together a really basic outline to talk fr...	01/05/2011 08:37:06 AM

From:	Matthew Klasen/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Date:	01/05/2011 08:37 AM
Subject:	Re: Feedback on press release

Ok -- I put together a really basic outline to talk from yesterday on the comments; I'll send that to you shortly if that helps.

(b) (5)

But just an idea. I could help find the "model" comments/responses while you're at FHWA.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water
(202) 566-0780
Cell (202) 380-7229

Christopher Hunter

----- Original Message -----
   From: Christopher Hunter
   Sent: 01/05/2011 08:31 AM EST
   To: Matthew Klasen
   Subject: Re: Feedback on press release
Thanks Matt.

Also, we've got the meeting this afternoon with Denise on the comments and responses, and I'm trying to put together a 1 pager of bullets to help frame the discussion. (b) (5) See what you think and edit as you like,

Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Matthew Klasen	I'll pick it up when I get in (about 20 min -- later t...	01/05/2011 08:28:38 AM

From:	Matthew Klasen/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Date:	01/05/2011 08:28 AM
Subject:	Re: Feedback on press release

I'll pick it up when I get in (about 20 min -- later than usual -- must be lack of sleep).

I'll scan them and send to you, Dave, and Denise, and leave the hard copy with Greg to make changes and re-send to OEA.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water
(202) 566-0780
Cell (202) 380-7229

   Christopher Hunter

  ----- Original Message -----
    From: Christopher Hunter
    Sent: 01/05/2011 08:15 AM EST
    To: Nancy Stoner
    Cc: David Evans; "Denise Keehner" <keehner.denise@epa.gov>; Matthew Klasen
    Subject: Re: Feedback on press release
Thanks Nancy,
Matt or I will be by later today to pick up the edits. Also, we should have a revised draft of the executive summary for your review later today or tomorrow morning.

Chris

Chris Hunter

U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Nancy Stoner	My proposed line edits will be on Martha's desk...	01/05/2011 07:44:53 AM

From: Nancy Stoner/DC/USEPA/US
To: "Denise Keehner" <keehner.denise@epa.gov>, David Evans/DC/USEPA/US@EPA, "Christopher Hunter" <Hunter.Christopher@epamail.epa.gov>
Date: 01/05/2011 07:44 AM
Subject: Feedback on press release

My proposed line edits will be on Martha's desk when I get in (by 9). Not difficult. Thx

Carrie Traver/R3/USEPA/US	To	Marcel Tchaou, Christopher Hunter
01/05/2011 05:09 PM	cc	Matthew Klasen, Stefania Shamet
	bcc	
	Subject	Reference List

Here is the latest reference list that I have. Items added or updated since the last list I sent out are in blue. The red items are spreadsheets of raw data.

I don't think Matt's "SAB report on conductivity from Dec. 28" on the list.

`ATTACHMENT REDACTED - DELIBERATIVE`

Revised Reference List.doc
Carrie Traver
USEPA Region 3
Office of Environmental Programs
1650 Arch Street - 3EA30
Philadelphia, PA 19103
215-814-2772
traver.carrie@epa.gov

Christopher Hunter	Good morning, Since Marcel is also in charge of...	01/05/2011 07:28:18 AM

From:	Christopher Hunter/DC/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Cc:	Carrie Traver/R3/USEPA/US@EPA
Date:	01/05/2011 07:28 AM
Subject:	Re: MORE References. Do we have these?

Good morning,

(b) (5)

Thanks
Chris Hunter
US EPA, Wetlands Protection Division
(202) 566-1454 (t)
(202) 573-6478 (c)

   Matthew Klasen

   ----- Original Message -----
      From: Matthew Klasen
      Sent: 01/04/2011 09:49 PM EST
      To: Stefania Shamet; Christopher Hunter
      Cc: Carrie Traver
      Subject: Re: MORE References. Do we have these?
Hey Stef,

Not sure what's best, and I'll defer to Chris, because I think Marcel has been working on the references appendix from HQ. But I think the non-piecemeal idea was a great approach.

In my comments to Kevin on 68A-113A, I noted the new SAB report on conductivity from Dec. 28 in a

couple responses, but didn't actually cite it directly -- so that's another one we can add to the list.

Thanks Carrie (and Stef, as always)!

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water
(202) 566-0780
Cell (202) 380-7229

To   Julia McCarthy

cc

bcc

Subject   Re: Spruce Exec Summary

Surprise, surprise, I've got something else. Can you read the latest draft of the SAB review panel's report on our conductivity benchmark for any Spruce-worthy tidbits. We might not be able to quote or cite it directly, but if there is anything you think is good stuff, let me know.

Thanks

SAB draft 12-28.pdf

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Julia McCarthy	SWEET! You're welcome for the turn around. L...	01/05/2011 03:44:09 PM

From:	Julia McCarthy/R8/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Date:	01/05/2011 03:44 PM
Subject:	Re: Spruce Exec Summary

SWEET! You're welcome for the turn around. Let me know if there's anything else you want me to work on...

Julia McCarthy (on detail)
Life/Environmental Scientist
U.S. Environmental Protection Agency
Office of Wetlands, Oceans and Watersheds
Wetlands Division
Washington, DC
(202) 566-1660
mccarthy.julia@epa.gov

Success is like wrestling a gorilla. You don't quit when you're tired. You quit when the gorilla is tired.
~Robert Strauss

-----Christopher Hunter/DC/USEPA/US wrote: -----

To: Julia McCarthy/R8/USEPA/US@EPA
From: Christopher Hunter/DC/USEPA/US
Date: 01/05/2011 03:38PM
Cc: Palmer Hough/DC/USEPA/US@EPA
Subject: Re: Spruce Exec Summary

(b) (5)

Chris

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Julia McCarthy---01/05/2011 12:55:01 PM---Hey Palmer,

From:	Julia McCarthy/R8/USEPA/US
To:	Palmer Hough/DC/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA
Date:	01/05/2011 12:55 PM
Subject:	Spruce Exec Summary

Hey Palmer,

Thanks,
Julia

Julia McCarthy (on detail)
Life/Environmental Scientist
U.S. Environmental Protection Agency
Office of Wetlands, Oceans and Watersheds
Wetlands Division
Washington, DC
(202) 566-1660
mccarthy.julia@epa.gov

Success is like wrestling a gorilla. You don't quit when you're tired. You quit when the gorilla is tired.
~Robert Strauss[attachment "Spruce ES - ch_jmm.doc" deleted by Christopher Hunter/DC/USEPA/US]

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chartered SAB, and does not represent EPA policy.

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7
8
9
10   EPA-SAB-11-xxx
11
12   The Honorable Lisa P. Jackson
13   Administrator
14   U.S. Environmental Protection Agency
15   1200 Pennsylvania Avenue, N.W.
16   Washington, D.C. 20460
17
18   Subject: Review of Field-Based Aquatic Life Benchmark for Conductivity in
19   Central Appalachian Streams
20
21   Dear Administrator Jackson:
22
23   The Mountaintop Mining Panel met on July 20-22, 2010 to review the Agency's draft
24   report, *A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams*.
25   The EPA document derives an aquatic life benchmark for conductivity, intended to protect 95%
26   of native genera in Appalachian streams exposed to mountaintop mining and valley fills. In the
27   enclosed report, we provide responses to the specific questions on the conductivity benchmark
28   posed in the Charge to the Panel.
29
30   Mountaintop mining and valley fills are important sources of stress to aquatic systems in
31   the Central Appalachian region, both from the perspective of localized and cumulative regional
32   impacts. In a companion report, the Panel provides a review of the full suite of impacts
33   associated with mountaintop mining and valley fills. There is clear evidence that valley fills are
34   associated with increased levels of dissolved ions (measured as conductivity) in downstream
35   waters, and that these increased levels of conductivity are associated with changes in the
36   composition of stream biological communities.
37
38   The SAB applauds the Agency's efforts to assess the linkages between measured levels
39   of conductivity and the presence or absence of native aquatic insects in Appalachian streams.
40   The field-based methodology for establishing a conductivity benchmark provides greater realism
41   than traditional laboratory-based methods because it includes native taxa and a range of life
42   stages. Although conductivity is a surrogate measure for the constituent ions that may contribute
43   to toxicity, the resulting benchmark provides a degree of protection comparable to, if not greater
44   than, a conventional water quality criterion based on traditional chronic toxicity testing.
45

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1 That said, the SAB Panel was concerned that the ecological effect was defined as loss of
2 an entire genus from a region, and was based only on common taxa. Another concern is that the
3 benchmark is based almost exclusively on data for aquatic insects, while the potential for
4 impacts on other rare and/or sensitive taxa (such as mollusks, fish, or water-dependent wildlife)
5 was not evaluated in setting the benchmark. Nor were changes in the abundance of taxa, short of
6 extirpation, considered. While the choice of ecological endpoints was dictated in part by the
7 availability of data, these choices may allow the loss of important and widespread aquatic taxa.
8
9 The extensive data set from West Virginia used to derive the benchmark provides broad
10 spatial coverage and includes a large number of streams with and without mountaintop mining
11 and valley fills. The similarity of the benchmark developed using an independent data set from
12 Kentucky was an important validation of the approach and the quality of the data. However, we
13 caution the Agency not to apply the conductivity benchmark beyond the environmental
14 conditions (e.g., geographic region, relative composition—or ionic signature—of the ions that
15 make up total conductivity) for which it has been validated.
16
17 The field-based approach for inferring stressor-response causality holds tremendous
18 promise for other regions (and other pollutants) if data sufficiency requirements are met. As
19 with conductivity, it will be important to assess potential confounding factors (i.e.,
20 environmental factors other than the stressor of concern) using multiple analytical approaches,
21 when establishing these causal relationships.
22
23 We appreciate the opportunity to review the technical documents relating to mountaintop
24 mining and valley fills and an associated conductivity benchmark. We look forward to your
25 response.
26
27
28 Sincerely,
29
30
31
32
33 Dr. Deborah L. Swackhamer   Dr. Duncan T. Patten
34 Chair   Chair
35 Science Advisory Board   Mountaintop Mining Panel
36
37 Enclosure

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1   **NOTICE**

2

3   This report has been written as part of the activities of the EPA Science Advisory Board (SAB),

4   a public advisory group providing extramural scientific information and advice to the

5   Administrator and other officials of the Environmental Protection Agency. The SAB is

6   structured to provide balanced, expert assessment of scientific matters related to problems facing

7   the Agency. This report has not been reviewed for approval by the Agency and, hence, the

8   contents of this report do not necessarily represent the views and policies of the Environmental

9   Protection Agency, nor of other agencies in the Executive Branch of the Federal government, nor

10   does mention of trade names of commercial products constitute a recommendation for use.

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1

2   # U.S. Environmental Protection Agency
3   ## Science Advisory Board
4   ## Panel on Ecological Impacts of
5   ## Mountaintop Mining and Valley Fills

6

7

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1
2 **Dr. Richard Warner**, University of Kentucky, Lexington, KY
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5 **SCIENCE ADVISORY BOARD STAFF**
6 **Ms. Stephanie Sanzone**, Designated Federal Officer, U.S. Environmental Protection Agency,
7 1200 Pennsylvania Avenue, NW (1400R), Washington, DC (sanzone.stephanie@epa.gov)
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2 # Science Advisory Board
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30 **Dr. David A. Dzombak**, Carnegie Mellon University, Pittsburgh, PA
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32 **Dr. T. Taylor Eighmy**, Texas Tech University, Lubbock, TX
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36 **Dr. John P. Giesy**, University of Saskatchewan, Saskatoon, Saskatchewan
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40 **Dr. James K. Hammitt**, Harvard University, Boston, MA
41
42 **Dr. Bernd Kahn**, Georgia Institute of Technology, Atlanta, GA
43
44 **Dr. Agnes Kane**, Brown University, Providence, RI
45

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1   **Dr. Madhu Khanna**, University of Illinois at Urbana-Champaign, Urbana, IL
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3   **Dr. Nancy K. Kim**, Health Research, Inc., Troy, NY
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5   **Dr. Catherine Kling**, Iowa State University, Ames, IA
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7   **Dr. Kai Lee**, David & Lucile Packard Foundation, Los Altos, CA
8
9   **Dr. Cecil Lue-Hing**, Cecil Lue-Hing & Assoc. Inc., Burr Ridge, IL
10
11   **Dr. Floyd Malveaux**, Merck Childhood Asthma Network, Inc., Washington, DC
12
13   **Dr. Lee D. McMullen**, Snyder & Associates, Inc., Ankeny, IA
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15   **Dr. Judith L. Meyer**, University of Georgia, Lopez Island, WA
16
17   **Dr. James R. Mihelcic**, University of South Florida, Tampa, FL
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19   **Dr. Jana Milford**, University of Colorado, Boulder, CO
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21   **Dr. Christine Moe**, Emory University, Atlanta, GA
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23   **Dr. Horace Moo-Young**, California State University, Los Angeles, CA
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25   **Dr. Eileen Murphy**, Rutgers University, Piscataway, NJ
26
27   **Dr. Duncan Patten**, Montana State University, Bozeman, MT
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29   **Dr. Stephen Polasky**, University of Minnesota, St. Paul, MN
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31   **Dr. Arden Pope**, Brigham Young University, Provo, UT
32
33   **Dr. Stephen M. Roberts**, University of Florida, Gainesville, FL
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35   **Dr. Amanda Rodewald**, The Ohio State University, Columbus, OH
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37   **Dr. Jonathan M. Samet**, University of Southern California, Los Angeles, CA
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39   **Dr. James Sanders**, Skidaway Institute of Oceanography, Savannah, GA
40
41   **Dr. Jerald Schnoor**, University of Iowa, Iowa City, IA
42
43   **Dr. Kathleen Segerson**, University of Connecticut, Storrs, CT
44
45   **Dr. Herman Taylor**, University of Mississippi Medical Center, Jackson, MS
46

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1   **Dr. Barton H. (Buzz) Thompson, Jr.**, Stanford University, Stanford, CA
2
3   **Dr. Paige Tolbert**, Emory University, Atlanta, GA
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5   **Dr. John Vena**, University of Georgia, Athens, GA
6
7   **Dr. Thomas S. Wallsten**, University of Maryland, College Park, MD
8
9   **Dr. Robert Watts**, Tulane University, Annapolis, MD
10
11   **Dr. R. Thomas Zoeller**, University of Massachusetts, Amherst, MA
12
13
14   **SCIENCE ADVISORY BOARD STAFF**
15   **Dr. Angela Nugent**, Designated Federal Officer, U.S. Environmental Protection Agency,
16   Washington, DC
17
18

1 **Table of Contents**

17

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chartered SAB, and does not represent EPA policy.

1. EXECUTIVE SUMMARY

The draft EPA document, *A Field-based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams*, March 2010 draft (USEPA, 2010a), defines a benchmark value for conductivity of streams. Conductivity is a measure of the electrical conductance in water, and is related to the major charged ions that are dissolved in waters. The benchmark conductivity value for streams in this region was determined to be 300 µS/cm, with 95% confidence bounds of 225 to 305 µS/cm. This value was developed using field data relating conductivity levels in streams with loss of aquatic insect genera. The benchmark is intended to protect 95% of aquatic taxa in streams in the Appalachian Region influenced by mountaintop mining and valley fill (MTM-VF). Using field measures of the presence or absence of macroinvertebrate (insect) genera and conductivity, the Agency calculated the conductivity concentration below which 95% of occurrences of a genus were observed. This value was termed the extirpation concentration (XC_{95}) because the genus was effectively not found in areas where conductivity exceeded that concentration. This procedure was repeated for genera that naturally occur in high quality (i.e., reference) sites within the study area, and the calculated XC_{95} values were used to construct a "species sensitivity distribution" (SSD) for macroinvertebrate genera. The conductivity benchmark is based on the hazardous concentration values at the 5th percentile of the SSD (the HC_{05}).

An extensive field data set from West Virginia was used to estimate the conductivity benchmark. A second, independent data set from Kentucky, where similar environmental conditions and MTM-VF occur, was used to validate the method. Applying the methodology to this second data set produced a benchmark value of 319 µS/cm, with 95% confidence bounds of 180 to 429 µS/cm.

The draft EPA document also describes the weight-of-evidence supporting a causal relationship between conductivity levels in Appalachian streams and the presence/absence of stream taxa. Causal criteria similar to those used in epidemiology were applied to the stressor-biological response relationship of concern. The report also summarizes analyses conducted to evaluate the potential that other environmental stressors (confounding factors) were contributing to observed patterns of genera occurrence.

The SAB Mountaintop Mining Panel (the Panel) met on July 20-22, 2010 to review the draft conductivity report, and held a follow-up public teleconference call on October 20, 2010. The Panel's responses to the charge questions are summarized below. (For the Panel's comments on the EPA document on the effects on aquatic ecosystems of mountaintop mining and valley fills, see the companion SAB report, EPA-SAB-11-xxx).

Adequacy of Data

The information used to develop the conductivity benchmark was derived from portions of two ecoregions (Ecoregions 69 and 70) in WV and KY, and these data were deemed adequate to establish a quantitative relationship between conductivity and benthic community responses in

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1 the sampled region. The primary sample set from WV provides broad spatial coverage and
2 includes a large number of streams with and without MTM-VF impacts. Therefore, the
3 relationships established between conductivity and the probability of extirpation for these genera
4 are relatively robust. The similarity of conductivity benchmarks derived from this analysis (300
5 µS/cm) and from an independent dataset from KY (319 µS/cm) provides an important validation
6 of the approach and the quality of the data, especially because data were collected by different
7 agencies using different techniques.

8   However, the background conductivity values at reference sites in the WV portions of the
9 two ecoregions were markedly different (75th percentiles were 110 and 198 µS/cm in Ecoregions
10 69 and 70, respectively). The EPA document should comment on the reason for these
11 differences between reference sites and discuss the extent to which a benchmark conductivity
12 value developed for Ecoregion 70 also would protect sensitive species in Ecoregion 69. Further,
13 the Panel recommends that the benchmark value not be applied to other areas of Ecoregions 69
14 and 70, beyond the boundaries of the geographic coverage of the current data set, without
15 additional validation.

16   One of the most important considerations for the proposed approach is the decision to use
17 extirpation of genera as an effects endpoint. The complete loss of a genus is an extreme
18 ecological effect and not a chronic response. Thus, a benchmark based on extirpation may not be
19 protective of the stream ecosystem. A "depletion concentration", defined as the level of a
20 stressor that results in a specified reduction in abundance, may be a more appropriate endpoint
21 than extirpation for development of a conductivity benchmark.

22   In addition, the Panel was concerned that only macroinvertebrate genera were used to
23 develop the benchmark. Although the WV database did not include fish, amphibians, or long-
24 lived macroinvertebrates such as mollusks, it would be instructive to compare the differential
25 response to conductivity among organisms such as these where possible. Rare species also were
26 excluded from the analysis. Rare species often are among the most sensitive taxa in a
27 community, and their elimination from the data pool could skew the results towards more
28 tolerant organisms.

29 **Field-Based Methodology**

30   The Panel agreed that the use of a field-based approach to developing the benchmark was
31 justified. Neither the approach nor the benchmark is perfect, but they provide improvement over
32 a benchmark that might have been derived from laboratory data using test species that are not
33 native to the region and do not reflect the broad range of life stage and life history strategies.
34 Thus, the benchmark likely provides a degree of protection comparable to or greater than a
35 conventional ambient water quality criterion derived from traditional chronic toxicity testing.
36 However, the Panel was concerned with the use of HC_{05} in the methodology. Accepting a loss of
37 5% of genera could eliminate entire groups of related species that are vulnerable to elevated
38 concentrations of particular dissolved ions for mechanistic reasons particular to their taxa. For
39 the streams in question, the HC_{05} would allow the loss of headwater genera (primarily mayflies)
40 that are common in unaffected streams, and that might be key to certain ecological functions.
41 Subject knowledge (e.g., from peer-reviewed literature on relevant stream ecosystems) could be

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1   employed to modify the benchmark if necessary to conserve important taxa of headwater
2   streams.

3   Multiple analytical approaches (e.g., quantile regression, logistic regression, conditional
4   probability analysis), as well as other study types (e.g., mesocosm and/or intensive site-specific
5   field investigations) could be used to support and complement field-based SSDs in a weight-of-
6   evidence approach.

7   Although the field-based approach is sound, the report would be improved by further
8   justification of the methodology and the chosen benchmark. For example, the report should
9   more clearly describe the many limitations with the extrapolation of laboratory data to nature. In
10   addition, the report should better support the use of conductivity as an indicator rather than the
11   concentration of particular ions or ion ratios. The report also should discuss the sensitivity of the
12   benchmark to the assumptions and constraints on the data set.

13   **Causality between Extirpation and Conductivity**

14   Building a strong case for causality between conductivity and loss of genera requires that
15   two linkages be demonstrated: (1) a strong relationship between stream conductivity and the
16   amount of MTM-VF in the upstream catchment, and (2) a strong relationship between elevated
17   stream conductivity and loss of benthic macroinverterate taxa. The EPA document presents a
18   convincing case for both linkages. To further strengthen the scientific basis for the benchmark,
19   the Panel recommends that the document include more information on the constituent ions that
20   contribute to conductivity at the sampled sites, and on the likely mechanisms of extirpation
21   produced by the constituent ions.

22   **Confounding Factors**

23   The report has done a credible job in isolating the major, potential confounding factors
24   and providing a basis for their assessment relative to the potential effect of conductivity.
25   However, the report would be strengthened by further attention to potential confounding factors
26   such as selenium and other trace metals, dissolved organic carbon, and hydrologic flows.
27   Further use of quantitative statistical analyses would be helpful for understanding causality and
28   the potential role of confounding factors.

29   **Uncertainty in the Benchmark**

30   The Panel commends the Agency for providing a characterization of the uncertainty in
31   the benchmark, reflected in the XC_{95} values, but suggests that the EPA document provide
32   additional detail on how the confidence bounds were generated. In addition, the document
33   should note other categories of uncertainty in the benchmark (e.g., uncertainties in the
34   assignment of cause and effect) that are not included.

35   **Comparing the Benchmark to Chronic Endpoints**

36   The Panel found that the general approach, including the use of field data and the
37   resulting benchmark, is sound and provides a degree of protection comparable to or greater than

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1   a conventional ambient water quality criterion derived from traditional chronic toxicity testing
2   because the approach includes native taxa and a range of life stages (i.e., early and late instar
3   larvae, and adults). The field-based benchmark is probably more reflective of changes in the
4   invertebrate community in response to changes in conductivity than would be chronic toxicity
5   tests. The XC_{95} approach used in this report provides useful and ecologically sound insights;
6   however, the choice of extirpation as an endpoint and the exclusion of rare taxa may result in a
7   loss of sensitivity.

8   **Transferability to Other Regions and Other Pollutants**

9   The Panel concluded that the field-based method used to develop the conductivity
10   benchmark was quite general and sufficiently flexible to allow the approach (though not the
11   benchmark value) to be transferred to other regions with different ionic signatures, where
12   minimum data requirements are met. These conditions include availability of high quality
13   reference sites, a common regional generic pool, similar levels of background conductivity and
14   ionic composition across the region, and a large field data set. The approach also seemed
15   applicable to other stressors—particularly where there is a relatively direct physiological
16   mechanism and effect linking the stressor and the occurrence of taxa—where data coverage and
17   quality are complete. However, change points in taxa abundances might be the more appropriate
18   choice for SSD statistics than an extirpation curve.

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2. INTRODUCTION

2.1. Background

EPA's Office of Research and Development (ORD) requested that the Science Advisory
Board (SAB) review the Agency's draft reports entitled *The Effects of Mountaintop Mines and
Valley Fills on Aquatic Ecosystems of the Central Appalachian Coalfields* (draft Aquatic
Ecosystem Effects Report) and *A Field-based Aquatic Life Benchmark for Conductivity in
Central Appalachian Streams* (draft Conductivity Benchmark Report; USEPA 2010a). The
reports were developed by ORD's National Center for Environmental Assessment at the request
of EPA's Office of Water (OW) and Regions 3, 4, and 5, to provide scientific information to
support a set of actions EPA is undertaking to clarify and strengthen environmental permitting
requirements for Appalachian surface coal mining operations.

In a detailed guidance memorandum (dated April 1, 2010), EPA lays out steps to be taken
by EPA Regions and states to strengthen permit decision-making for Appalachian surface coal
mining activities. The memorandum notes that the two technical documents mentioned above
are being sent to SAB for review. In the interim, the memorandum provides guidance on the
interpretation of narrative Water Quality Criteria for elevated conductivity, such that projects
resulting in "predicted conductivity levels below 300 µS/cm generally will not cause a water
quality standard violation and that in-stream conductivity levels above 500 µS/cm are likely to
be associated with … exceedences of narrative state water quality standards." The memorandum
also notes that the Agency will evaluate whether changes to these conductivity benchmarks are
appropriate, based on the results of the SAB review.

The Panel met on July 20-22, 2010 to review and provide advice to ORD on the scientific
adequacy, suitability and appropriateness of the two ORD reports. The Panel reviewed the draft
reports and background materials provided by ORD, and considered public comments and oral
statements that were received. The Panel held a follow-up public teleconference on October 20,
2010. The Panel's advice is provided in two SAB advisory reports. The present document
provides advice on the Conductivity Benchmark Report and a companion SAB report (EPA-
SAB-11-XXX) discusses the draft Aquatic Ecosystem Effects Report.

2.2. Charge to the Panel

The Agency's Charge to the Panel (Appendix A) included a total of 14 questions, of
which the following 8 relate to the Conductivity Benchmark Report:

Charge Question 1: The data sets used to derive a conductivity benchmark were
developed primarily by two central Appalachian states (WV and KY). Please comment
on the adequacy of these data and their use in developing a conductivity benchmark.

Charge Question 2: The derivation of a benchmark value for conductivity was adapted
from EPA's methods for deriving water quality criteria. The water quality criteria
methodology relies on a lab-based procedure, whereas this report uses a field-based

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1   approach. Has the report adapted the water quality criteria methodology to derive a water
2   quality advisory for conductivity using field data in a way that is clear, transparent and
3   reasonable?
4
5   Charge Question 3: Appendix A of the EPA report describes the process used to
6   establish a causal relationship between the extirpation of invertebrate genera and levels of
7   conductivity. Has the report effectively made the case for a causal relationship between
8   species extirpation and high levels of conductivity due to surface coal mining activities?
9
10   Charge Question 4: In using field data, other variables and factors have to be accounted
11   for in determining causal relationships. Appendix B of the EPA report describes the
12   techniques for dealing with confounding factors. Does the report effectively consider
13   other factors that may confound the relationship between conductivity and extirpation of
14   invertebrates? If not, how can the analysis be improved?
15
16   Charge Question 5: Uncertainty values were analyzed using a boot-strapped statistical
17   approach. Does the SAB agree with the approach used to evaluate uncertainty in the
18   benchmark value? If not, how can the uncertainty analysis be improved?
19
20   Charge Question 6: The field-based method results in a benchmark value that the report
21   authors believe is comparable to a chronic endpoint. Does the Panel agree that the
22   benchmark derived using this method provides for a degree of protection comparable to
23   the chronic endpoint of conventional ambient water quality criteria?
24
25   Charge Question 7: As described, the conductivity benchmark is derived using central
26   Appalachian field data and has been validated within Ecoregions 68, 69, and 70. Under
27   what conditions does the SAB believe this method would be transferable to developing a
28   conductivity benchmark for other regions of the United States whose streams have a
29   different ionic signature?
30
31   Charge Question 8: The amount and quality of field data available from the states and the
32   federal government have substantially increased throughout the years. In addition, the
33   computing power available to analysts continues to increase. Given these enhancements
34   in data availability and quality and computing power, does the Panel feel it feasible and
35   advisable to apply this field-based method to other pollutants? What issues should be
36   considered when applying the method to other pollutants?

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1   # 3. Response to Charge Questions

2

3   ## 3.1. Adequacy of Data

4   *Charge Question 1: The data sets used to derive a conductivity benchmark were developed*
5   *primarily by two central Appalachian states (WV and KY). Please comment on the*
6   *adequacy of these data and their use in developing a conductivity benchmark.*

7

8   The information used to develop the conductivity benchmark was derived from portions
9   of two ecoregions (Ecoregions 69 and 70) in WV and KY[1], and these data were deemed adequate
10   to establish a quantitative relationship between conductivity and benthic community responses in
11   the sampled region. The EPA document suggests (e.g., pages xiii and 20, and Figure 1) that the
12   benchmark may be applicable to the entirety of Ecoregions 69 and 70, including portions in OH,
13   PA, TN and MD. However, as discussed below, the Panel recommends that the benchmark not
14   be applied outside the geographic bounds of the current data set without further validation
15   because of differences in the background conductivity levels in other portions of these
16   ecoregions.

17   Sample sites were excluded from the analysis if they were collected from large rivers or
18   had ionic concentrations or composition markedly different from those typically associated with
19   mountaintop mining and valley fills (MTM-VF). The authors also removed sites with low pH ($<$
20   6) from the analysis before identifying extirpation concentrations. Some of these decisions limit
21   the generality and broad applicability of the conductivity benchmark, but they are appropriate to
22   ensure that the relationships developed were a function of elevated conductivity and not spurious
23   correlations. The decision to omit data from sites where organisms were not identified to genus
24   also is appropriate and further enhances the quality of the results; Pond et al. (2008) reported that
25   data based on family-level identification were less effective for distinguishing effects associated
26   with high conductivity downstream from MTM-VF areas. In addition, the EPA document
27   correctly notes that there may be significant variation in sensitivity among species within the
28   same genus and that these differences should be considered when assessing effects associated
29   with elevated conductivity.

30   A total of 2145 samples (from an initial sample of 3286 sites) with macroinvertebrate and
31   conductivity data met the acceptance criteria and were evaluated from these two ecoregions.
32   This sample set provides broad spatial coverage and includes a large number of streams with and
33   without MTM-VF impacts. Therefore, the relationships established between conductivity and
34   the probability of extirpation for these genera are relatively robust. The similarity of
35   conductivity benchmarks derived from this analysis (300 µS/cm) and from an independent
36   dataset from KY (319 µS/cm) provides an important validation of the approach and the quality of
37   the data, especially because data were collected by different agencies using different techniques.

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[1] The KY data set used for validation also included samples from a small portion of Ecoregion 68.

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1   The EPA document states that the WV and KY datasets are well-documented, regulatory
2   databases with excellent quality assurance. However, more information on the specific methods
3   used to sample water conductivity and macroinvertebrates would help in evaluating the quality
4   of these data. For example, were conductivity measurements standardized and reported at 25
5   °C? For macroinvertebrates, were quantitative or semi-quantitative techniques employed? What
6   mesh size was used in the field and laboratory? Were macroinvertebrate samples sub-sampled,
7   and if so how many organisms were removed? Details of sampling protocols are provided in the
8   WVDEP reports cited. However, because these methodological details are essential for
9   evaluating the quality of these data, they also should be provided in EPA's conductivity
10   benchmark report.

11   Data from Ecoregions 69 (Central Appalachia) and 70 (Western Allegheny Plateau, or
12   WAP) were selected because of the high quality of data (water quality and macroinvertebrates),
13   because the region is currently undergoing significant MTM-VF impacts, and because the two
14   ecoregions have similar water quality and biota. However, the background conductivity values
15   at reference sites in the two ecoregions were markedly different (75th percentiles were 110 and
16   198 µS/cm in Ecoregions 69 and 70, respectively[2]). The EPA document should comment on the
17   reason for these differences between reference sites. For example, do they reflect differences in
18   underlying geology between central Appalachia and the Allegheny Plateau? More importantly,
19   do these differences in background conductivity affect macroinvertebrate responses? Is it
20   possible to estimate HC_{05} values from these 2 ecoregions separately? In other words, would a
21   benchmark conductivity value developed for Ecoregion 70 also be protective of sensitive species
22   in Ecoregion 69?

23   Even within an ecoregion, it is important to consider whether natural background levels
24   of conductivity are homogeneous enough to derive a single benchmark value for that ecoregion.
25   In the Ohio portion of Ecoregion 70, for example, water hardness related to conductivity is
26   higher relative to the datasets from the KY and WV portions of the ecoregion (see Figure 1,
27   below). In addition, a study of a random subset of wadeable reference sites supported the
28   generally higher background conductivity (mean of 416 µS/cm) in the Ohio portion of Ecoregion
29   70 (Figure 2) compared to southern parts of the ecoregion. These data suggest that most
30   reference sites in the WAP ecoregion in OH would have conductivity values greater than the 300
31   µS/cm benchmark developed using WV data. For subregions with high natural background
32   conductivity, the genera that comprise the species sensitivity distribution (SSD) might need to be
33   screened to account for the fact that genera associated with low conductivity/low hardness
34   conditions would not be expected at reference sites in those areas.

35

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[2] Although the draft review document reports 75th percentiles of 100 and 234 µS/cm in Ecoregions 69 and 70, EPA
staff indicated that the correct values are 110 and 198 µS/cm, respectively.

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CONCENTRATION OF HARDNESS AS CALCIUM CARBONATE,
IN MILLIGRAMS PER LITER

Mean hardness as calcium carbonate at NASQAN water-monitoring sites during 1975 water year.
Colors represent site data representing streamflow from the hydrologic-unit rea.
(Map edited by USEPA, 2005)

Figure 1. Data illustrating concentration of hardness across the United States. Note the elevated water hardness in southeast Ohio compared to Kentucky and West Virginia within Ecoregion 70.
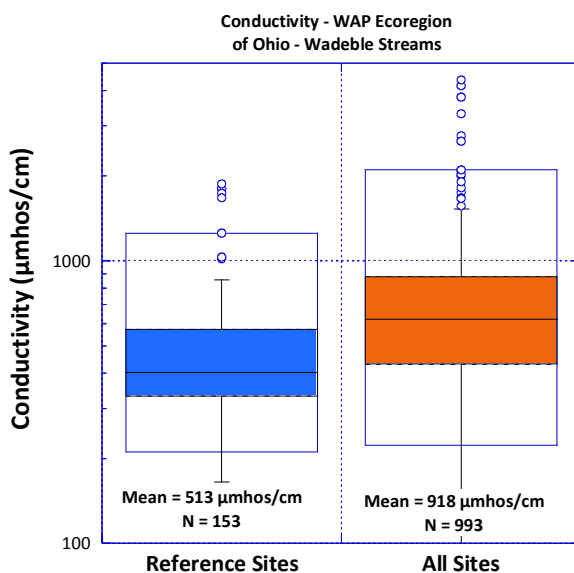
Figure 2. Box plot of conductivity at Ohio least impacted wadeable reference sites (left) and all sampling sites (right) in the WAP ecoregion of Ohio. (Figure modified from Amaning, 2006; Data obtained from Ohio EPA.)

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1

2   Figure 3 shows plots of two sensitive genera (Leptophlebia and Ephemerella) sampled in
3 areas within the Ohio portion of the WAP ecoregion that have, on average, higher stream
4 conductivity. These plots are similar to those in Figure D-1 of the EPA document, where the y-
5 axis is the probability of occurrence of taxa along a gradient of conductivity generated by
6 dividing the samples into 20 equal-sized bins and the midpoint of conductivity represents the
7 mean conductivity within that bin of data. Although the pattern of decline is similar for the WV
8 and OH data, the concentrations are shifted to the right. This suggests that XC_{95} values may be
9 higher if calculated from Ohio data[3].

10   Thus, the conductivity benchmark derived using data from WV may not be applicable to
11 areas beyond the geographic bounds of the dataset, and the benchmark should not be applied to
12 other portions of the ecoregions without further validation. Figure 1 in the EPA document
13 should be revised so that the shaded area labeled "Advisory Area" is restricted to the sampled
14 region. Furthermore, the figure caption is misleading, and should be revised to note that data
15 used to develop the benchmark are from the WV portion of Ecoregions 60 and 70, not from the
16 full ecoregions (which span the states of PA, KY, TN, WV and MD). (See Section 3.7, response
17 to Charge Question 7, for discussion of the applicability of the method to other regions.)

18

19

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[3]The Ohio data set includes some species-level data within these genera, and might permit differential sensitivity
between species to be tested and perhaps sub-ecoregion classifications could be examined. In addition, the Ohio
biological criteria were derived for tiered aquatic life uses (TALUs) and derivation of conductivity or other stressor
benchmarks could vary with the probability of different genera occurring among different aquatic life tiers.

1
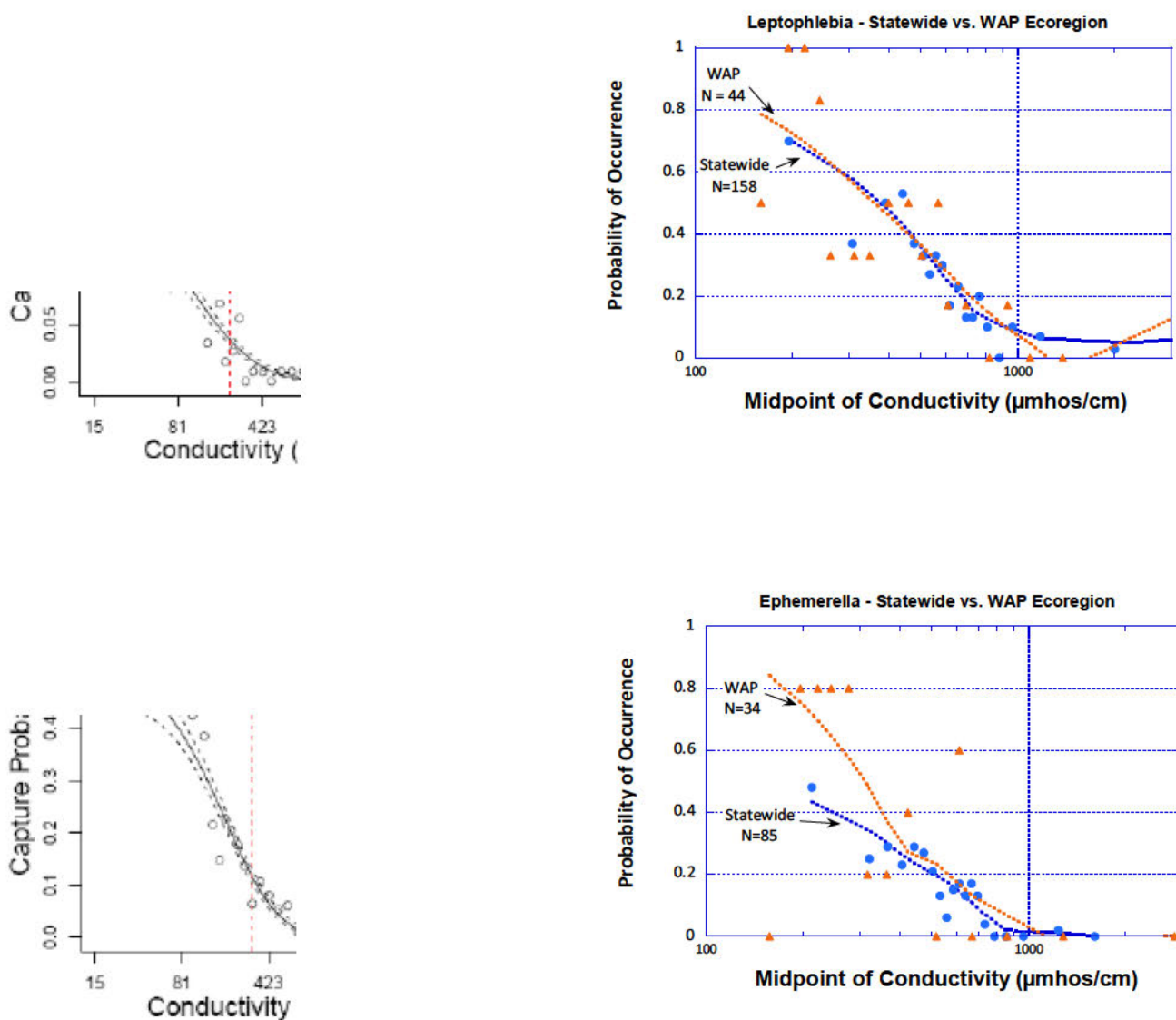
Figure 3. Observation probabilities for two genera of aquatic insects used in the EPA conductivity benchmark report -- Leptophlebia (upper left) and Ephemerella (lower left) and similar plots generated for Leptophlebia in Ohio (statewide and WAP ecoregion, upper right) and Ephemerella in Ohio (statewide and WAP ecoregion, lower right). (Data for right-most figures from Ohio EPA)

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1   The decision to exclude rare genera (i.e., those that occurred at fewer than 30 sites) is a necessary
2   practical decision. However, it would be appropriate to acknowledge that rare taxa are often
3   important for biological assessments (Cao et al., 1998) and may be more sensitive to elevated
4   conductivity. Species are rare for many reasons, but one of the reasons is greater sensitivity to
5   environmental stressors (Clements and Newman, 2002). The document also should provide a
6   specific justification for using < 30 sites as the cutoff point for inclusion of genera in the
7   analysis. Is this a minimum amount of data necessary to generate a statistically rigorous species
8   sensitivity distribution (SSD)?

9   One of the most important considerations for the proposed approach to develop a
10 conductivity benchmark is the decision to use genera extirpation as an effects endpoint. This
11 issue is briefly addressed in Section 5.8 of the EPA report, but it requires additional
12 consideration from EPA. Unlike laboratory-derived SSDs, which are based on chronic responses
13 (e.g., growth, reproduction) or acute lethality (e.g., LC_{50} values), the field-based approach
14 defines an adverse effect as the loss of a genus from a stream. The complete loss of a genus is an
15 extreme ecological effect and not a <u>chronic</u> response. Congeneric species can have vastly
16 different environmental requirements and sensitivities; thus, levels of any stressor need to be
17 relatively high before an entire species or genus is eliminated from a site. Therefore, as noted in
18 Section 5.8 of the EPA report, a benchmark based on extirpation may not be protective of the
19 stream ecosystem. A "depletion concentration", defined as the level of a stressor that results in a
20 specified reduction in abundance, may be a more appropriate endpoint for development of a
21 conductivity benchmark. (Additional discussion of extirpation as an endpoint is presented in
22 Section 3.6, response to Charge Question 6.)

23   A large data set was available for the development of a conductivity benchmark for the
24 region. However, the data apparently lack flow (volume/time) measurements and the EPA
25 document should clarify that data were collected only from perennial streams, and not
26 intermittent or ephemeral streams. A future effort to collect data on ephemeral streams (which
27 flow only in response to rainfall/runoff) is needed to fill the gap in data for these systems**.** A
28 second concern with the data set is the temporal distribution of the samples – Table 2 of the EPA
29 document gives a general breakdown, but the report should provide additional detail on month
30 and/or season of sampling. If, for example, most of the mined sites were sampled in late spring
31 as opposed to early spring, impacts on insect emergence (which is related to degree day
32 accumulations) might be missed.

33   A series of reports published by the USDA Forest Service and EPA (Dyer, 1982a; 1982b;
34 1982c) provide additional water quality data from first-order streams in the Appalachian coal
35 fields, including conductivity data from unmined and mined first-order streams and watersheds.
36 While the Forest Service data do not include benthic samples, conductivity values (and other
37 parameters) from unmined sites would certainly expand the data on background conductivity
38 levels in the region.

39   The Panel was concerned that only macroinvertebrate genera were used to develop the
40 benchmark. Although the WV database did not include fish, amphibians, or long-lived
41 macroinvertebrates such as mollusks, it would be instructive to compare the differential response
42 among organism such as these where possible.

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1   The EPA document should describe the process for defining data quality objectives
2   (DQOs) and intended uses for the conductivity benchmark following, for example, EPA's
3   systematic planning and DQO process (U.S. EPA 2006). Although it is clear that the
4   conductivity benchmark is intended to provide an indication of macroinvertebrate impairment
5   connected to a causal variable, how this benchmark will be used, for example in regulatory
6   programs, is not well defined. This is important because the intended uses of the benchmark
7   may influence the degree of uncertainty that is tolerable or acceptable to decision-makers. If the
8   DQOs associated with benchmark derivation are defined to fit existing data rather than first
9   designing a field program necessary to achieve a set of objectives, then the resulting benchmark
10   may not protect the true 5th percentile genus from adverse impacts, which is the primary
11   objective of EPA's current aquatic life criteria development guidelines (Stephan et al., 1985).

12   In ideal circumstances, the data used for the conductivity benchmark would come from
13   highly controlled laboratory studies using macroinvertebrate species common to the Appalachian
14   coal-mining region or, in their absence, from a carefully executed project designed to produce
15   field data as a substitute. In the case presented here, it appears that the objective of developing
16   an aquatic life benchmark is being adapted to a macroinvertebrate data set used as part of a
17   Stream Condition Index (SCI) tool to evaluate biological impairment of aquatic life use (see
18   Pond et al., 2008, page 718). Nonetheless, developing the benchmark using pre-existing field
19   data gathered in the MTM-VF region is a reasonable, timely, and cost-effective approach. This
20   assumes, of course, that: (1) the QA/QC measures associated with the studies at the source of the
21   data were adequate (few details are given); (2) enough data were available even after culling out
22   data that were confounded for one reason or another; and (3) the source studies for the data
23   contained adequate reference sites. These assumptions appear to be largely met, although more
24   information regarding QA/QC would be helpful to put the data into perspective.

25   **3.2. <u>Field-Based Methodology</u>**

26   *Charge Question 2: The derivation of a benchmark value for conductivity was adapted*
27   *from EPA's methods for deriving water quality criteria. The water quality criteria*
28   *methodology relies on a lab-based procedure, whereas this report uses a field-based*
29   *approach. Has the report adapted the water quality criteria methodology to derive a*
30   *water quality advisory for conductivity using field data in a way that is clear,*
31   *transparent and reasonable?*
32
33   The Panel agreed that the use of a field-based approach to developing the benchmark was
34   justified. Neither the approach nor the benchmark is perfect, perhaps because they borrow too
35   much from the traditional approach, but they provide improvement over a benchmark that might
36   have been derived from laboratory data using test species that are not native to the region and do
37   not reflect the broad range of life stage and life history strategies. However, there were a number
38   of areas where the report did not sufficiently justify the choices made and/or explain why a field-
39   based approach was a better choice than the traditional laboratory approach.

40   **The field-based approach was justified but not perfect.** The goal of the EPA report
41   was to develop a benchmark to protect benthic communities from adverse effects associated with
42   elevated conductivity, and this goal was clearly stated. One of the criticisms raised in the public

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1 comments on the field-based approach was that the final data set used in the analysis is highly
2 caveated, using about 10 different criteria to narrow the data set to circumstances where major
3 confounding variables are minimized. Constraining the data set is statistically justified in this
4 case because eliminating obvious confounding situations was the most reasonable way to
5 establish a benchmark that is minimally confounded by other stressors. The result is a
6 benchmark that is relevant to effects associated with conductivity

7   However, the Panel was concerned about the use of HC_{05} in the methodology, an
8 approach directly derived from the traditional laboratory approach. Accepting a loss of 5% of
9 genera could have the effect of eliminating entire groups of related species that are vulnerable to
10 elevated concentrations of particular dissolved ions for mechanistic reasons particular to their
11 taxa. For the streams in question, the HC_{05} would allow the loss of headwater genera (primarily
12 of mayflies) that are common in unaffected streams, and that might be key to certain ecological
13 functions. Better application of subject knowledge—for example, of key attributes of the
14 undisturbed communities and the role of taxonomic components in important ecosystem
15 functions—could be employed to modify the benchmark if necessary to conserve many food-
16 web-important taxa of headwater systems that have XC_{95} values less than 300 µS/cm. A field-
17 based methodology is particularly suited to the use of subject knowledge to protect key taxa (that
18 are sensitive to elevated ion concentrations). It is not a methodology used in the traditional
19 laboratory-based approach because the use of surrogate species in toxicity testing is not suitable
20 to understanding sensitivities of native species. In this case, deviation from the traditional
21 approach is both justified and recommended.

22   **Compare field-based benchmarks derived from multiple approaches**. The use of
23 field data to derive benchmarks for stressor identification or TMDL development has been
24 relatively widespread, although the methods have varied widely. In a recent review of a draft
25 EPA document, *Empirical Approaches for Nutrient Criteria Derivation*, another SAB panel
26 recommended that stressor-response relationships be evaluated using multiple analytical
27 approaches (e.g., ordinary least squares regression, quantile regression, logistic regression,
28 conditional probability analysis, and other other quantitative methods) and a "weight-of-
29 evidence" approach (U.S. EPA SAB 2010). In the context of the conductivity benchmark, a
30 similar approach might be useful whereby targets developed by multiple approaches would at a
31 minimum lend support to the benchmarks derived using the field-derived SSD.

32   Some of the other methodologies employ data used as indicators or metrics (e.g., EPT
33 taxa) in state programs that can provide a level of comfort with results of the field-derived SSD
34 methodology. State decision-making thresholds (for Section 401 permitting, determining
35 attainment or impairment of aquatic life uses, etc.) often are tied directly to biological
36 benchmarks. Demonstration of the links between the field-derived benchmarks discussed here
37 and assemblage benchmarks used by state programs could influence how a state applies the
38 proposed conductivity benchmarks. Benchmark values for TMDL development or stressor
39 identification have been derived using field data by a number of states and more comparisons
40 with these methodologies would be very useful.

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1   **The report should provide clear, complete and transparent justification of the**
2 **methodology and the chosen benchmark.** There are several areas where it is important that the
3 clarity and justification of the approach and benchmark be improved.

4   • The report appropriately references the 1985 guidelines approach, and recognizes the
5   common aspects of the two approachs; for example, the use of species sensitivity
6   distributions. However, it is critical to transparency that the report better (and more
7   explicitly) describe, or perhaps list in one place, the differences in the approach**.**
8

9   • A new methodology based on field data will come under especially heavy scrutiny.
10   Therefore, the report should more clearly describe the many limitations in extrapolating
11   from a laboratory approach to nature and reasons why field-based approaches, or a
12   combination of laboratory and field-based approaches, are preferred. Field data usually
13   include more taxa and more system-relevant taxa than can be achieved in laboratory tests.
14   In particular:
15

16   o Traditional laboratory surrogates (often crustaceans) are not suitable for testing
17   the effect of changing major ion concentrations. Mayflies and other groups are
18   especially sensitive because of common traits probably associated with
19   osmoregulation. Crustaceans, however, employ a different approach to
20   osmoregulation that makes them much less vulnerable to high concentrations of
21   major ions. For this reason, a field-based approach to develop a conductivity
22   benchmark is preferable to one based on laboratory tests using *Ceriodaphnia*, for
23   example, which would be under-protective and misleading.

24   o Routine testing protocols do not yet exist for the native species most sensitive to
25   high conductivity. Laboratory studies use species biased towards culture;
26   culturing methodologies do not exist yet for the species most sensitive to high
27   conductivity. Thus good methods for deploying a laboratory approach are not
28   available for evaluating potential toxicity associated with elevated conductivity.
29

30   • The report needs to be more explicit, and/or complete, in justifying the use of
31   conductivity as an indicator rather than particular ions or ion ratios. EPA should make a
32   strong case up front for how conductivity directly relates to key ionic stressors such that
33   it can be a surrogate for those parameters. (In Section 3.3, the Panel suggests additional
34   information that could be included on this topic.)
35

36   • The report could include examples relating conductivity to other aquatic effect endpoints
37   (other than mayflies) to further strengthen the conclusions.

38   • As mentioned in the previous section, the report should be clear about the extent to which
39   the data come from perennial streams only. However, the empirical relationship between
40   conductivity and genera occurrence likely would be applicable to intermittent (but not
41   ephemeral) streams in the WV area because intermittent streams have a component of
42   base flow, the traits of vulnerable species are common to all stream types, and because of
43   connected downstream influences. (Note: the Panel is not commenting on whether the

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1   legal jurisdiction of the NPDES permit program should include perennial or intermittent
2   streams.)

3   •   The report should discuss the effect on the benchmark of each assumption used to
4   constrain the data set, including a summary of the sensitivity of the outcome to these
5   constraints and assumptions (i.e., how alternative approaches or assumptions would alter
6   the benchmark). Apparently some of this analysis has already been done by EPA but was
7   not presented in the report. While the Panel understands the Agency's desire to keep the
8   report of manageable length, a sensitivity analysis of this sort could be presented in
9   summary tables or figures and perhaps in an appendix where more discussion is
10   necessary. Examples of questions that could be considered include:

11   o   What is the effect on the benchmark if the requirements for excluding rare species
12   are relaxed?
13   o   What is the effect on the benchmark of including genera that do not appear at the
14   reference sites?
15   o   How would adjustments to the choice of season affect the benchmark?
16   o   What is the effect on the benchmark of including fish data (at least using examples
17   from the small data sets available), so as to address the Stephan et al. (1985) goal
18   of including all the fauna in the benchmark?
19   o   Would a different benchmark result if the nutrient numerical limit methods
20   recently released by USEPA (U.S. EPA 2010b) were used as an alternative?
21   o   What is the effect if individual major ions (suspected toxins) or ratios are included
22   instead of conductivity, where data are available?
23   o   How does the benchmark change if abundance-weighted analyses are used instead
24   of presence/absence?
25   o   How would quantile regression affect the choice of benchmark?
26
27   •   Appendix E of the EPA document should provide additional detail on the analysis of
28   data from Kentucky that is used to support the validation of the conductivity benchmark
29   and the field-based approach. The authors apparently conduct a similar data analysis
30   process with an apparently similar data set and obtain "similar results" in terms of a
31   derived conductivity benchmark. The appendix includes XC_{95} values for all genera
32   (Tables E-3 and E-4) and presents results of SSDs for all-year, spring and summer
33   sampling periods (Figure E-2 and E-3). However, the appendix does not contain a
34   results/discussion section. Consequently, the authors seem to proceed directly from a
35   discussion of methods to a conclusion that the method is "robust." Also, no causal
36   analysis is presented in Appendix E. This is a critical element in support of the
37   conductivity benchmark, and it should be repeated as a part of the validation of the
38   approach.
39
40   **Additional guidance is required on the conditions under which the conductivity**
41 **benchmark is applicable to a stream**. In the EPA document, the authors note repeatedly (e.g.,
42 p. xii, xiii, 1, 2, 4, 6, 19, 20) that the "aquatic life benchmark for conductivity is applicable for
43 streams *in the Appalachian Region where conductivity is dominated by salts of SO_4^{2-} and*
44 *HCO_3^{-} at circum-neutral to mildly alkaline pH* [emphasis added]." Such constraints on the

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1 applicability of the benchmark are very important, but are not adequately defined in the
2 document. In fact, the report never quantifies the percentage of conductivity generated by
3 individual ions or compounds such as sulfate or bicarbonate, a method that would be required to
4 assess the "dominant" contributors to conductivity. Rather, the report apparently uses
5 concentration thresholds, rather than dominance of conductivity as stated, to establish
6 applicability of the benchmark. This issue is presented only in the context of stream site data
7 that were excluded from developing the benchmark. For example, Page 6 of the EPA report
8 states that: "[Data] were excluded if the salt mixture was dominated by Cl^- rather than SO_4^{2-}
9 (conductivity > 1000 µS/cm, SO_4^{2-} < 125 mg/L, and Cl^- > 250 mg/L)." Similarly, the required
10 "circum-neutral" pH range is not defined explicitly. This is only presented in the context of
11 stream site data that were excluded from developing the XC_{95} values in the consideration of
12 confounding variables – with stream site data that were excluded if pH < 6, and no mention of an
13 upper pH bound. Additionally, background conductivity levels in some areas of the Appalachian
14 Region may limit applicability of the benchmark (see discussion in Section 3.1). Overall, the
15 criteria to establish applicability of the benchmark and methodology need to be defined explicitly
16 and clarified.

17   The EPA report should highlight that comparing values of concentration in mass units
18 (e.g., mg/L) for different ions is *not* a valid way to compare their quantities or to assess which
19 constituents are dominant. Concentrations in mass units (e.g., mg/L) are useful in practical
20 application and are used for values for drinking water standards, toxicity limits, etc, but they
21 should *not* be used when quantifying relationships between concentration and conductivity.
22 Given the focus here on conductivity -- ability of water to conduct an electric current – defining
23 concentrations in equivalent units (e.g., µeq/L) is appropriate. Equivalent weight units
24 (calculated as the formula weight divided by the electrical charge) incorporate the chemical
25 behavior of a solute; one equivalent is the amount of ion required to cancel out the electrical
26 charge of an oppositely charged monovalent ion. Thus, the Panel recommends that Figure 1
27 (page 24), Figure 11a-e (Pages 36-40) and related information in the EPA report aiming to show
28 relations among ions and conductivity be re-cast in equivalent units (e.g., µeq/L) rather than
29 mass units (mg/L). An excellent reference providing information on how to convert water
30 chemistry units is provided by Hem (1985). Further, it is important that information on
31 ions/compounds that dominate conductivity be presented as the percent of conductivity made up
32 by these individual constituents. The amount of conductivity generated by an equivalent unit of
33 sulfate is very different than the amount of conductivity generated by an equivalent unit of
34 chloride or bicarbonate. This can be done by calculating the *equivalent ionic conductance* of
35 each of the individual matrix ions, and their contributions to the overall conductance of the water
36 solution (e.g., following Laxen 1977, with summary tables presented by Boyd 2000).

37   To illustrate the importance of these comments, data are provided for 40 forested,
38 headwater streams in central Pennsylvania, relatively unimpacted by human activities, with
39 about half located in the Appalachian region of Ecoregions 67 and 70 (Table 1, below).
40 Information on concentration (table -left) portrays a very different picture of the importance of
41 individual ions when compared to information on the percent of conductivity they generate
42 (table-right). In these streams there is not a single one where the fraction of conductivity
43 generated by (sulfate + bicarbonate) is greater than 50%; rather, conductivity is dominated by the
44 other ions.

Table 1. Conductivity and Ion Concentrations in 40 Headwater Pennsylvania Streams During Summer Base Flow (Source: E. Boyer, unpublished data)

	Conductivity			Matrix Ions - concentrations								Matrix Ions - % contribution to total conductivity								
--	uS/cm	% from matrix ions		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	%	%	%	%	%	%	%	%	
Code			pH	SO4	DIC	NO3	Cl	Ca	Mg	Na	K	SO4	HCO3	Cl	NO3	Ca	Mg	Na	K	so4+hco3
BB21	203 6	99 4	7 0	8 7	1 5	0 8	58 2	5 9	1 9	24 6	1 0	5	3	47	0	8	5	31	1	8
BB14	100 2	99 6	6 4	12 7	0 7	3 2	19 0	3 5	2 4	6 5	1 8	17	2	34	3	11	13	18	3	19
BB27	174 7	99 6	7 4	8 0	7 3	3 9	32 9	10 5	4 3	12 1	2 3	5	18	29	2	16	11	16	2	23
BB12	89 7	99 7	6 7	12 4	1 8	1 1	15 0	5 0	1 9	5 9	1 2	17	7	28	1	17	10	17	2	24
BB33	59 1	99 7	7 2	8 6	2 1	1 4	4 2	6 3	1 0	2 1	0 9	18	16	12	2	32	8	9	2	34
BB15	75 2	99 7	6 7	17 9	1 2	1 6	8 1	3 7	1 9	4 1	1 3	30	5	18	2	15	13	14	3	35
BB2	47 3	99 8	6 8	9 7	1 5	1 5	3 5	4 8	1 1	0 9	0 5	25	12	12	3	30	11	5	2	37
BB20	126 4	98 7	7 0	19 2	6 6	0 6	10 6	10 9	3 3											
										5 8	1 4	18	19	13	0	24	12	11	2	37
BB22	233 5	99 8	7 7	16 8	17 2	1 4	28 1	18 7	4 5	16 0	2 5	8	30	17	0	20	8	15	1	37
BB11	189 8	99 6	7 1	49 1	3 5	1 4	15 1	17 1	6 1	5 7	1 3	30	7	13	1	25	15	7	1	38
BB36	106 8	99 9	6 9	11 0	7 5	1 5	5 3	10 5	2 6	4 5	1 2	12	26	8	1	28	12	10	2	38
BB3	94 6	99 2	7 0	19 8	3 1	1 5	7 4	7 9	2 4	2 9	0 9	26	13	13	1	25	12	8	1	39
BB37	121 3	99 7	7 6	8 5	9 5	2 5	8 5	12 7	2 9	4 6	1 5	8	32	10	2	27	10	9	2	40
BB34	58 9	99 6	6 7	13 4	5 6	1 6	4 7	7 5	2 4	3 3	0 9	19	22	9	2	25	13	9	2	40
BB29	210 1	99 6	7 8	20 6	16 7	5 3	12 0	24 9	7 2	7 3	1 4	10	30	8	2	28	14	7	1	40
BB35	23 2	99 7	7 0	3 3	1 7	1 4	0 8	2 4	0 8	0 4	0 4	15	26	5	5	27	15	4	2	41
BB8	49 8	98 6	7 5	8 2	2 6	0 9	3 3	5 1	1 1	1 0	0 6	19	22	10	2	29	10	5	2	41
BB38	137 0	99 0	7 9	5 8	13 0	3 0	4 0	21 5	2 3	2 8	1 1	4	38	4	2	39	7	4	1	42
BB24	22 1	99 6	6 2	7 1	0 4	0 3	0 9	2 0	0 6	0 6	0 4	39	3	6	1	26	12	7	3	42
BB31	214 1	99 9	7 8	12 3	21 8	0 9	16 2	23 4	6 9	8 7	2 4	6	37	10	0	25	12	8	1	43
BB6	68 6	99 9	7 4	13 2	2 8	1 3	3 7	6 2	1 1	2 2	0 7	24	19	9	2	27	8	8	2	43
BB25	220 8	99 4	7 9	24 3	16 8	1 3	10 6	24 6	5 8	7 5	2 0	12	32	7	0	29	11	8	1	44
BB13	110 1	98 5	7 4	14 6	8 0	4 0	4 7	10 1	3 6	2 3	1 4	15	29	6	3	25	15	5	2	44
BB19	25 9	99 9	6 6	7 3	0 7	0 3	0 8	2 2	0 6	0 7	0 4	36	9	5	1	26	12	7	3	45
BB1	44 1	99 6	6 8	11 2	1 8	1 1	1 2	4 6	1 1	0 5	0 5	31	14	5	2	31	12	3	2	45
BB4	81 1	99 9	7 3	14 7	5 0	3 2	1 5	11 2	1 4	0 4	0 9	20	25	3	3	37	8	1	2	46
BB7	255 2	99 9	8 0	21 1	25 0	3 6	11 3	29 3	7 0	8 7	2 7	8	38	6	1	27	11	7	1	46
BB16	198 5	99 9	7 6	19 8	18 6	1 4	12 4	17 9	5 3	8 5	2 4	10	36	9	1	22	11	9	2	47
BB23	49 6	99 4	7 6	10 7	2 6	0 9	1 5	5 8	1 0	0 8	0 7	24	23	4	2	32	9	4	2	47
BB9	220 6	99 8	7 5	20 1	21 5	1 3	11 0	21 2	5 3	8 3	2 9	10	38	7	0	24	10	8	2	48
BB32	199 2	99 1	8 0	5 1	24 7	6 0	3 3	30 0	6 1	1 7	0 7	2	45	2	2	34	11	2	0	48
BB5	109 7	99 4	7 5	16 0	7 8	1 2	4 7	8 9	3 2	2 6	1 3	17	31	7	1	23	14	6	2	48
BB18	158 9	99 7	7 0	16 4	16 8	0 4	4 9	16 0	4 7	3 3	2 3	11	37	4	0	26	13	5	2	48
BB10	56 7	99 6	7 4	12 2	3 0	1 7	1 1	6 7	0 8	0 4	0 7	26	23	3	3	34	7	2	2	49

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1 **3.3. <u>Causality Between Extirpation and Conductivity</u>**

2 <u>*Charge Question 3*</u>*: Appendix A of the EPA report describes the process used to establish a*
3 *causal relationship between the extirpation of invertebrate genera and levels of*
4 *conductivity. Has the report effectively made the case for a causal relationship between*
5 *species extirpation and high levels of conductivity due to surface coal mining?*

6
7   To build a strong case for causality, two linkages must be demonstrated: (1) a strong
8 relationship between stream conductivity and the amount of MTM-VF in the upstream
9 catchment, and (2) a strong relationship between elevated stream conductivity and loss of benthic
10 macroinvertebrate taxa.

11 **Linking stream conductivity and the amount of MTM-VF in the upstream catchment**

12   The EPA document makes a convincing case that stream conductivity increases below
13 valley fills and that the greater the valley fill extent, the higher the level of conductivity. The
14 authors further make a convincing case that high conductivity waters dominated by sulfate and
15 bicarbonate, but low chloride, are associated with mining activity. Both natural (e.g.,
16 weathering-related) and anthropogenic (e.g., atmospheric deposition) sources of conductivity
17 exist, even in areas unimpacted by mining. However, the correlation analysis and Figure A-3 in
18 the EPA document show convincing support for a very strong signal between the percent valley
19 fill and conductivity (dominated by sulfate and bicarbonate), while the same analyses show weak
20 relationships between conductivity and other potential suspect variables (e.g., percent forest,
21 percent urban).

22 **Linking elevated stream conductivity and loss of benthic macroinvertebrate genera**
23
24   The general consensus of the Panel is that a convincing case has been made relating
25 elevated conductivity and extirpation of invertebrate genera. While the analyses primarily focus
26 on the mayflies (Ephemeroptera), supporting evidence from other groups was also included (as
27 shown in Fig.s A-1, A-2 of the EPA report). The authors demonstrated a negative correlation
28 between conductivity and the number of Ephemeroptera genera, and to a lesser extent, the total
29 number of genera. These correlations held when sites with elevated levels of potential
30 confounders were removed. The EPA document presents a plausible physiological mechanism
31 for the effect of exposure to elevated concentrations of ions (i.e., the need for freshwater
32 invertebrates to maintain internal osmotic pressure and ion balance in dilute media; the presence
33 of specialized ionoregulatory cells or tissues in some insect orders; the dependence of other
34 physiological processes on ion balance). The data demonstrate consistency in patterns of loss of
35 specific taxa associated with elevated conductivity; in the present study and another published
36 study, similar groups of genera were the most sensitive to conductivity. Finally, the authors
37 made a case for sufficiency, i.e., that exposed taxa experienced a sufficient magnitude of
38 exposure to elicit an effect (but see comments below). For example, effect levels for *Isonychia*
39 spp. from the literature were similar to the XC_{95} for that genus in the present study.

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1   In the absence of major confounders, the field-based data are more indicative of actual
2 responses because the organisms are exposed to the potential stressor throughout their entire
3 lives, and they show an integrated effect that accounts for the potential for additional stress that
4 laboratory studies simply cannot mimic.

5   Although we believe the authors have made a strong case linking elevated conductivity
6 and extirpation of genera, there are a number of important points and recommendations to
7 consider:
8

9 • Conductivity itself is not a pollutant, but is a surrogate measure for the major
10   constituent ions in the mixture. Thus, the supporting information presented by the
11   authors may be representative of a combination of effects of the constituent ions.
12   Furthermore, if there are unaccounted for factors that may be confounding the causal
13   relationship between stress from specific ions and taxa loss (e.g., dietary selenium
14   exposure or slight reductions in habitat quality), conductivity may still be interpreted
15   as a signal for the presence of the combination of factors resulting from the presence
16   of upstream VF. The EPA document should include more information on the likely
17   mechanisms of extirpation produced by the constituent ions because stress is not due
18   to conductivity itself, but rather is linked to volume regulation, ion regulation and
19   osmoregulation. There is a rich literature on this central physiological theme and
20   reference to this literature will further strengthen the case for conductivity as a
21   reliable surrogate measure (e.g., see Nemenz 1960; Gainey and Greenberg, 1977;
22   Schoffeniels and Gilles, 1979; Kapoor 1979; Pierce 1982; Dietz et al., 1998; Scholz
23   and Zerbst-Boroffka, 1998). In addition, data figures in the document showing SSD
24   as a function of conductivity would be enhanced by the inclusion of a second x-axis
25   that indicates a metric of ionic strength or other measure more directly related to
26   osmotic/ionic/volume stress.

27 • Mixture calculations can be made to better understand the role and contribution of the
28   constituent ions. EPA's Environmental Monitoring and Assessment Program
29   (EMAP) has information on how to calculate percent contribution to conductivity
30   from the various ionic constituents (<u>reference please</u>). Mixture decomposition
31   calculations may help to guide the transferability of the method to regions with
32   differing ionic signatures. Indeed, the EPA report should provide data to show the
33   variability in the relative proportions of $SO_4{}^{2-}$ and $HCO_3{}^-$ at the field sites in the
34   current study. However, the relationships between conductivity and specific ions in
35   the current report all appear to be strong and similar in distribution, suggesting that
36   ion ratios are relatively similar across the sites.

37 • The authors should take care to ensure that literature studies selected to support
38   "Sufficiency" in the analysis are drawn from areas with similar ionic signatures to the
39   advisory area. Supporting data for conductivity effect levels were based on
40   potassium salts, which are not present in important concentrations in the West
41   Virginia system. As stated above, going outside the ecotoxicological literature to the
42   ionoregulation literature may provide supporting evidence.

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1   •   We also caution the authors on the interpretation of evidence with respect to
2   "Alteration" (Section A.2.4 in the EPA document). The effect is consistent, but
3   perhaps not so specific. Metals may produce a similar effect (i.e., loss of mayfly
4   genera).

5   3.4. <u>Addressing Confounding Factors</u>

6   *Charge Question 4: In using field data, other variables and factors have to be accounted for*
7   *in determining causal relationships. Appendix B of the report describes the techniques for*
8   *dealing with confounding factors. Does the report effectively consider other factors that may*
9   *confound the relationship between conductivity and extirpation of invertebrates (genera)? If*
10   *not, how can the analysis be improved?*
11

12   The Panel commends the authors for carefully considering factors that may confound the
13 relationship between conductivity and extirpation of invertebrate genera. This was accomplished
14 by: (1) removing some potentially confounding factors from the data set before determining the
15 benchmark concentrations; and (2) considering weight-of-evidence of a suite of other potentially
16 confounding factors that were not excluded from the data set – using correlations between
17 potential confounding factors, conductivity, and aquatic genera (mayflies). The report has done
18 a credible job in isolating the major, potential confounding factors and providing a basis for their
19 assessment relative to the potential effect associated with conductivity.

20   The use of mayflies as the aquatic response variable in the analyses of confounding
21 factors was appropriate. It would be helpful to reiterate in Appendix B that the hypothesis that
22 conductivity is the primary variable explaining patterns of mayfly taxonomic richness was
23 addressed earlier (in Appendix A of the EPA document), and that this hypothesis could not be
24 rejected due to weight of evidence.

25   The Panel emphasizes the importance of clarifying the relationship between conductivity
26 and the matrix ions that generate conductivity. The document as a whole has not provided
27 sufficient clarity regarding the relative importance of conductivity (i.e., the effect of
28 salinity/ionic strength on an organism's ionic balance) versus specific ionic constituents as causal
29 variables. This contributes to the lack of clarity in whether an individual constituent (e.g.,
30 sulfate), total ionic strength, or some other single or combination of chemicals is the most
31 appropriate causal factor. Further, questions remain about the potential effect on aquatic life of
32 minor constituents that do not greatly shape conductivity, including organics (e.g., dissolved
33 organic carbon), trace metals (e.g., iron, aluminum, zinc) and trace minerals (e.g., selenium).

34   Given the content of the public comments, the treatment of confounding factors may well
35 be one of the most critical parts of the benchmark report. Thus, the Panel recommends that the
36 report be strengthened by considering the following additions:

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1   •   Address additional potential confounding factors, including further attention to selenium
2   and other trace metals, dissolved organic carbon, and flows.

3   o   Trace metals and minerals (e.g., selenium) and organic matter (e.g., dissolved
4   organic carbon) may not contribute substantially to the conductivity of
5   freshwaters, but are tightly linked to other changes in flow and water quality.
6   o   Flow conditions and base flows also may influence conductivity levels; in some
7   cases high flow is associated with high conductivity (particularly if sulfate
8   predominates) and in other cases high flow is associated with low conductivity
9   (more likely if bicarbonate dominates the system) (e.g., see Geidel 1979).
10   o   Several panelists suggested the potential importance of the undisturbed
11   hyporheos, noting that the survivorship of larval forms depends on an extant,
12   vibrant hyporheos and this was not covered, *per se*, in the report.
13   o   A more detailed analysis of substrate composition and vegetation, factors known
14   to greatly affect macroinvertebrate communities, would improve the analysis of
15   macroinvertebrate responses to conductivity levels and potential confounding
16   factors.
17

18   •   Consider further use of quantitative statistical analyses for understanding causality and
19   the potential role of confounding factors. Because parametric procedures have been used
20   successfully elsewhere to evaluate multivariate environmental data sets and can provide a
21   relatively objective, quantitative framework for data analysis, a more rigorous statistical
22   analysis should be contained in the document. Further, it would be helpful for the
23   authors to clarify whether nonparametric multivariate methods, such as non-metric
24   multidimensional scaling, were considered.

25 **3.5. <u>Uncertainty in the Benchmark</u>**

26   *<u>Charge Question 5</u>: Uncertainty values were analyzed using a boot-strapped statistical*
27   *approach. Does the SAB agree with the approach used to evaluate uncertainty in the*
28   *benchmark value? If not, how can the uncertainty analysis be improved?*

29   The Panel commends the Agency for providing a characterization of the uncertainty in
30 the benchmark, reflected in the XC_{95} values. Several authors (Barnett and O'Hagan, 1997;
31 Reiley et al., 2003; Hope et al., 2007) describe the need for and value of quantitative expressions
32 of uncertainty in water quality criteria and guidance values (a water quality "benchmark" in this
33 case). Benefits include improved characterization and communication of the reliability of a
34 criterion; more realistic risk assessments; more frequent inclusion of uncertainty into decision-
35 making; and a better appreciation of the potential for a criterion to be over- or under-protective
36 (Reiley et al., 2003).

37   The bootstrap resampling approach appears to be sound and consistent with techniques
38 found in peer-reviewed literature. Bootstrapping is commonly used in environmental studies to
39 estimate confidence limits of a parameter, and the method has been used in the estimation of
40 HC_{05} values (e.g., Newman et al., 2000). However, in addition to the reference to Efron and
41 Tibshirani (1993), it would be helpful for the document to briefly discuss other examples of the
42 use of bootstrapping in relevant water resources applications.

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1   In addition, certain aspects of the approach are not sufficiently clear. For example, with
2   the ranges of the confidence intervals for the 35 genera shown in Figure 7 of the EPA report,
3   how is the interval reported for the benchmark (confidence interval of 95-305 µS/cm about the
4   benchmark of 300 µS/cm) derived? We recommend that the authors provide a more detailed
5   description of the method used, with both narrative and figures, detailing how to generate the
6   bootstrap means/confidence intervals for each genus of interest, and how the data generated from
7   the bootstrapping procedure is used to derive confidence limits on the proposed benchmark.
8   Some discussion also is needed of why 1000 was selected as the appropriate number of
9   resamples. What were the trade-offs between the reliability/repeatability of the confidence limits
10 versus a larger number of resampling events? Although 1000 is commonly used to derive
11 bootstrap confidence limits, the reader may benefit from more discussion of the basis for this
12 choice.

13   Finally, although confidence limits for the benchmark that reflect uncertainty and
14 variation in the extirpation data are important and useful, there are other uncertainties in the
15 benchmark that are not assessed using the bootstrap resampling procedure. For example,
16 uncertainties in the assignment of cause and effect between specific conductance and
17 macroinvertebrate extirpation are not reflected in the confidence limits. The authors state in
18 Section 3.4 (Confidence Bounds) that "[T]he purpose of this analysis is to characterize the
19 statistical uncertainty in the benchmark value," and in Section 4.4 (Uncertainty Analysis), the
20 authors discuss sources of uncertainty that are and are not reflected in the derived confidence
21 limits. This discussion is important to the utility of the document and to other uses of this
22 approach. It may be helpful to describe more clearly in Section 4.4 what is meant by "statistical
23 uncertainty" and we recommend that the authors ensure that this topic is addressed clearly and
24 comprehensively.

25 **3.6. <u>Comparing the Benchmark to a Chronic Endpoint</u>**

26   *Charge Question 6: The field-based method results in a benchmark value that the report*
27   *authors believe is comparable to a chronic endpoint. Does the Panel agree that the*
28   *benchmark derived using this method provides for a degree of protection comparable to the*
29   *chronic endpoint of conventional ambient water quality criteria?*
30
31   The general approach, including the use of field data and the resulting benchmark, is
32 sound and provides a degree of protection comparable to or greater than a conventional ambient
33 water quality criterion derived from traditional chronic toxicity testing. The field-based
34 benchmark is probably more reflective of how the invertebrate community responds to
35 conductivity than would be chronic toxicity tests. One reason is that chronic toxicity tests
36 usually involve abbreviated times of exposure (relative to generation times of species) and they
37 use surrogate species. Furthermore, as noted in Section 3.2 above, the surrogate species most
38 commonly employed to study effects of conductivity (e.g., crustaceans like *Ceriodaphnia dubia*)
39 are not especially sensitive to changes in major ion concentrations for physiological reasons.
40 The species most sensitive to conductivity are often very difficult to work with in demanding
41 tests like chronic toxicity tests. The ability to focus on the most sensitive groups of species in
42 the constrained field data set is a powerful connection to reality that routine toxicity testing
43 cannot achieve. In this sense, the result is a benchmark that is probably more sensitive to

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1 changes in conductivity than would be a benchmark dependent upon traditional chronic toxicity
2 testing, but also one more realistic in terms of protecting invertebrate communities in streams
3 affected by MTM-VF.

4 The XC$_{95}$ approach used in this report provides useful and ecologically sound insights.
5 The specific manner in which the SSD approach was applied (i.e., using field survey data from
6 impacted locations) is reasonable and avoids many of the flaws of laboratory test-based SSD
7 analyses that ignore fundamental concepts of synecology (Luoma 1995). The Executive
8 Summary (page xii) of the EPA document states that "SSDs represent the response of aquatic life
9 as a distribution with respect to exposure. It is implicitly assumed that if exposure level is kept
10 below the 5th percentile of the SSD, at least 95% of species will be protected." Although this
11 assumption is frequently stated, it is not ecologically supported (e.g., see Hopkin 1993; Newman
12 and Clements, 2008, pp. 205-208), is not needed to support the report's conclusions, and should
13 be omitted from the document.

14 As noted previously, the report could be improved if it more explicitly confronted the
15 issues surrounding use of laboratory testing to estimate ecological effects. Such tests ignore
16 aspects like physiological acclimation in extrapolation to the field. Laboratory tests are done
17 with individuals of a specific demographic class of a single species exposed to constant
18 concentrations without any co-stressor(s) for durations of somewhat arbitrary length. In contrast,
19 the survey data have exceptional ecological realism and provide a stronger basis for inferring
20 causality between concentrations of one or more constituent ions (using conductivity as a
21 surrogate measure) and presence/absence of genera in aquatic communities in streams below
22 MTM-VF activities.

23 The approach based on field surveys seeks "the level of exposure above which a genus is
24 effectively absent from water bodies in the region." The extirpation concentration (XC) is the
25 95% point of the surveyed data distribution. The data sets are large enough to allow good
26 estimation. Correctly, the EPA document notes that "this level is not fully protective of rare
27 species…" (page 8, lines 11-19). In fact, it is possible that the benchmark will not protect a
28 number of mayflies important to small streams in this region. The arbitrary choice to protect
29 95% of genera is partly mitigated by constraining the data set, so as to protect 95% of genera
30 highly sensitive to increased conductivity.

31 The choice of extirpation as an endpoint results in a loss of sensitivity (as compared to
32 employing a 50% decline in abundance, for example). The Agency might consider incorporating
33 into the endpoint a safety factor, subject knowledge, or some other protocol for added protection.
34 On the other hand, the benchmark already approaches the background during the period of
35 highest conductivity in reference streams, and the method includes steps (removal of data that
36 could be confounding) that enhance its sensitivity compared to published approaches. The
37 concern about loss of abundant species speaks to the importance of a regional understanding of
38 impacts (e.g., what is the spatial scale of the extirpation?) and the difficulty of managing risk on
39 a stream-by-stream basis in a region where several thousand miles of streams are already
40 impaired by mining.

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1   The approach relative to the data bins and weights seems reasonable. The nonparametric
2   approach and CI estimation methods are sound. As a minor point, it would be good to clarify on
3   Page 10 (lines 14 and 24) whether "removed" and "trimmed" are synonymous. Usually, they are
4   not. Also, on Page 11 (line 7), although the applied estimation of proportion [R/(N+1)] is
5   acceptable and commonly used, a better approximation of proportion from ranks is provided by
6   the Blom approximation, (R-0.375)/(N+0.25) (Looney and Gulledge, 1985).

7   As noted previously, rare species are not included in the SSD, nor are classes of
8   organisms like fish. Some method to address the influence on the benchmark of rare species or
9   addition of non-insect species is warranted. In this regard, freshwater mussels are a concern as
10   they are a unique feature of the area's biodiversity, are often listed as threatened or endangered,
11   and are poor volume/ionic/osmotic regulators. Focusing on one sensitive group of invertebrates
12   (Ephemeroptera) might limit the persuasiveness of the benchmark in risk management, and
13   thereby make it less defensible. Recognizing that conductivity is a surrogate for one set of
14   stressors (dissolved ions), it is important to include in the overall impact analysis of MTM-VF
15   more of the factors that contribute to the cumulative stress (e.g., risks to mussels, risks to the
16   broader food web from selenium), as discussed in the Panel's companion report on the aquatic
17   ecosystem effects of MTM-VF (see EPA-SAB-11-XX).

18   **3.7. <u>Transferability of the Method to Other Regions</u>**

19   *Charge Question 7. As described, the conductivity benchmark is derived using central*
20   *Appalachian field data and has been validated within Ecoregions 68, 69, and 70. Under*
21   *what conditions does the SAB believe this method would be transferable to developing a*
22   *conductivity benchmark for other regions of the United States whose streams have a*
23   *different ionic signature?*
24
25   The consensus of the Panel was that the field method used to develop the conductivity
26   benchmark was quite general and sufficiently flexible to allow the approach (though not the
27   benchmark value) to be transferred to other regions with different ionic signatures, where
28   minimum data requirements are met. (Note: Despite the wording of Charge Question 7, the
29   Panel emphasizes that the conductivity benchmark of 300 µS/cm has been validated only for
30   <u>portions</u> of Ecoregions 68, 69 and 70, and recommends that the benchmark not be applied
31   beyond the geographic bounds of the data set without additional validation.)

32   For application to a new region, the Panel suggests that the following important
33   conditions should be met:

34   **1) High quality reference sites should be available.**

35   The current approach requires that all genera included in calculation of a benchmark for a
36   region must occur at least once at a reference site (as well as be found at 30 or greater sampling
37   sites). In general, high quality streams have greater biodiversity than low quality streams. Thus,
38   availability of high quality reference sites lends itself to a longer list of genera available for the
39   analysis that, in turn, enables the benchmark to be based on a broader baseline of generic
40   extirpation data. The presence of reference sites also provides a baseline of minimally disturbed

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1   sites for use in deriving background conductivity levels. Ideally, these reference sites should be
2   geographically wide-spread in order to adequately represent all portions of the study region. The
3   Panel notes, however, that reference sites are not an absolute requirement because some areas
4   may be so modified by historic human activity that no true reference exists. When reference
5   sites are not available, minimally disturbed locations may need to be used as surrogates for
6   "reference sites."

7   **2) Fauna found at reference sites in the region should reflect a common regional**
8   **generic pool.**

9   Macroinvertebrate species differ significantly from one another in their degree of
10 pollution tolerance or intolerance. Although congeneric species can differ, differences in
11 sensitivity to stressors are particularly evident when comparing species from different genera or
12 families. On this basis, macroinvertebrates have been assigned meaningful pollution
13 tolerance/intolerance values using best professional judgement, based on a combination of data
14 from field distributions and laboratory tests (e.g., Lenat 1993). Thus, a representative sample of
15 genera from across the region of interest is necessary to develop a benchmark for protecting
16 biodiversity of streams. Failure to capture a common pool may exclude some important taxa.

17 **3) There should be good prior knowledge and understanding of the environmental**
18 **requirements of the regional pool of genera.**

19 Good prior knowledge lends credibility to the overall process because it can assure that
20 the benchmark is based on a group of genera representing a broad gradient of pollution
21 tolerance/intolerance across the region (e.g., reflecting differences across genera in physiology,
22 phylogenetic origin, trophic position in the foodweb, and life history characteristics). This
23 breadth in genera, in turn, assures that the benchmark will be representative and afford broad
24 protection for the streams in the region.

25 **4) Background levels of conductivity should be similar across reference sites in the**
26 **region.**

27 Similarity in background conductivity levels across the set of reference sites decreases
28 the possibility of misinterpretation resulting from confounding factors. The degree of variation
29 in conductivity among minimally disturbed sites also serves as a logical consistency check. If
30 some reference sites have very high conductivity, either the organisms are not responding
31 negatively to conductivity or the site is misclassified.

32 **5) Relative ionic composition (ratio of ions) of the elevated conductivity should be**
33 **consistent across the region.**

34 Specific ions contributing to conductivity (e.g., Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, HCO_3^-, CO_3^{-2},
35 SO_4^{-2}) differ in their relative toxicity to macroinvertebrates in general, as well as their relative
36 toxicity to individual genera. Therefore, consistency in the proportion of ions in the mixture will
37 make it easier to defend conductivity as a surrogate. As long as the ratio of ions constituting
38 conductivity is consistent across the region, then the relative sensitivity of each genus to a given
39 level of conductivity also will be consistent across the region. If the ratio of ions varies

26

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1 appreciably, then a given level of conductivity may be toxic to a particular genus in one stream
2 but not in another (because one stream has a higher proportion of an ion that is more toxic to the
3 genus in question).

4 **6) The potential confounding factors for the region should be understood and**
5 **addressed.**

6 Confounding factors are variables in the test region that co-occur with conductivity.
7 Confounders can interfere with the ability to accurately model the relationship between level of
8 conductivity and occurrence of genera because confounding variables may also affect genera
9 occurrence. A few examples of confounding variables include temperature, pH, selenium, and
10 habitat quality. To be credible, the benchmark needs to be non-confounded or the confounding
11 factor also must be a result of mountaintop mining and valley fills. There are many ways that a
12 given factor can be a confounding variable, and many ways of weighting those factors.
13 Regardless, a process needs to be in place to vet each factor for its potential as a confounding
14 variable and eliminate any field data that might be confounded prior to developing the
15 benchmark. The process used in Appendix B of the conductivity benchmark report provides a
16 framework that can be applied in other regions. However, multiple analytical approaches (e.g.,
17 quantile regression, logistic regression, conditional probablility analysis, and/or other statistical
18 procedures) also should be used in a weight-of-evidence approach to addressing potential
19 confounding factors.

20 **7) A large field data set should be available.**

21 One of the strengths of the benchmark development process for WV was the wealth of
22 available data. Specifically, the data set involved a large number of genera, which occurred
23 across an array of sites representing a broad gradient of conductivity levels. Thus, even after
24 removing genera because they were too rare or removing sites because they were confounded by
25 factors such as low pH, there still remained a critical mass of data to derive the benchmark.
26 (Note: A sensitivity analysis performed on the existing WV/ KY data set might provide insights
27 into the minimum sample size needed to assure an acceptable level of variance around the
28 benchmark.)

29 **8) A second, independent data set should be available for the region to validate the**
30 **benchmark, but if not available, some other approach for validating the benchmark**
31 **should be used.**

32 Validation of the benchmark is extremely important to gain widespread acceptance of its
33 use and to assess uncertainty in the value, and thus the potential for the benchmark to be either
34 overly or insufficiently protective of the environment. Ideally, validation would involve a
35 separate calculation of the benchmark using a second independent dataset from the region, and
36 comparing the second value to that derived from the primary data set. In the absence of an
37 independent dataset, bootstrapping or other statistical methods (e.g., jackknifing) can be used to
38 estimate benchmarks for comparison and to provide an estimate of certainty around the original
39 value. For large data sets, a subset of the data might be held aside (i.e., not used to develop the

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1   benchmark) and used for validation. Sensitivity analysis should be used to determine the size of
2   this sample.

3   **9) The benchmark should not be extrapolated beyond the geographic bounds of the**
4   **data set unless sufficient data are available for validation.**

5   Application of the benchmark beyond the geographic bounds of the data set would be
6   difficult to defend for a variety of reasons. First, there would likely be less overlap in the
7   taxonomic composition (at the generic level) of the macroinvertebrate community of reference
8   sites located beyond the bounds of the region and this would confound the selection of taxa for
9   the analysis. Second, it is likely that the genera in streams located beyond the geographic bounds
10 would be different than the mix of genera (and hence different tolerances/intolerances for
11 conductivity) from which the benchmark was derived. Third, reference sites outside the
12 geographic bounds may differ in ionic chemistry to those within the bounds of the data set (e.g.,
13 dissimilar levels of pH, alkalinity, and hardness), and this would exert a confounding influence
14 due to the effect of acclimation chemistry on the toxicity level of a given compound on a genus.
15 Fourth, it is likely that the dominant source of ions (and thus the ionic composition) underlying
16 human induced, elevated conductivity would differ in streams far outside the geographic bounds
17 and confound the application of the benchmark.

18   As noted in Section 3.1, even within an ecoregion, the latitudinal (or longitudinal) span
19 may be so large that taxa and geologies are vastly different between the spatial extremities of the
20 region. If the region for which the benchmark is being developed is too large or too
21 geographically fragmented in terms of key habitat/topographic features, then there may be a
22 taxonomic gradient at the generic level across the region (i.e., streams in one part of the region
23 containing genera that are unique or distinct from those in other parts). These differences in
24 community structure, coupled with differences in the pollution tolerance/intolerance associated
25 with the different genera, confound the benchmark development effort. This makes equating
26 extirpation of a genus with a given concentration of the stressor (in this case, conductivity, as a
27 surrogate for dissolved ions from MTM-VF) problematic because it may be very difficult to
28 distinguish between a genus being extirpated due to the contaminant of concern versus
29 extirpation due to an overall change in habitat (which is unsuitable for the species represented by
30 that genus).

31

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1   **3.8. Transferability of the Method to Other Pollutants**

2   *Charge Question 8: The amount and quality of field data available from the states and the*
3   *federal government have substantially increased throughout the years. In addition, the*
4   *computing power available to analysts continues to increase. Given these enhancements in*
5   *data availability and quality and computing power, does the Panel feel it feasible and*
6   *advisable to apply this field-based method to other pollutants? What issues should be*
7   *considered when applying the method to other pollutants?*
8

9   Water quality criteria (WQC) have been a major component of the CWA Water Quality
10   Standards (WQS) programs and have provided the primary pollutant targets for management of
11   discharges to surface waters of the United States, particularly for toxicants from point source
12   dischargers regulated by NPDES discharge permits. The work in this document has extended the
13   laboratory methodology of Stephan et al. (1985) to a field-based methodology built around
14   generating SSDs for conductivity for taxa in a geographic region that have sufficient data to
15   generate extirpation statistics (n=30 data points), that occur in reference sites, and that are not
16   exotic (i.e., alien) species. The Panel concluded that the methodology can be translated to other
17   stressors with certain caveats, detailed below.

18   The SSD field methodology outlined in the EPA report provides key advantages over a
19   sole reliance on laboratory results. First, the Panel recommends that, where possible, the
20   derivation of such benchmarks should be broadly determined and include consideration of all
21   suitable data that can illuminate the responses of species or taxa to a stressor. Such an effort,
22   depending on the stressor, could include applicable standard laboratory test results (which would
23   demonstrate the sensitivity of some species), results from more novel controlled approaches
24   (e.g., mesocosm studies) and robust field-based biological and stressor data. The Panel felt that
25   the advantages of using field data for deriving the conductivity benchmark could apply to many
26   other stressors, although the specific considerations and caveats may differ from those addressed
27   in the Panel's report.

28   As the EPA report noted, the laboratory testing approach has been successful and most
29   amenable to toxicants (e.g., ammonia, metals) with clear and consistent modes of effect. Some
30   stressors, particularly naturally occurring compounds (e.g., nutrients) and habitat-related
31   stressors, have proven less tractable to the standard laboratory approach used to derive
32   benchmarks (Stephan et al., 1985). Salinity, for example has a strong natural gradient of
33   occurrence (i.e., ranging from saltwater to streams with low hardness and low dissolved solids).
34   Expected impacts of salinity on taxa depend greatly on natural geological and soil conditions,
35   which are key biogeographic determinants of the distribution of species adapted to and native to
36   a particular salinity regime. Natural background concentrations of dissolved materials vary
37   geographically, as does the composition of the ions and anions that comprise the total dissolved
38   solids. Indeed, the EPA report emphasizes that the initial application of the conductivity
39   benchmark should be limited to three ecoregions and for regions "dominated by salts of SO_4^{2-}
40   and HCO_3^- at circum-neutral to mildly alkaline pH." The Panel further cautions its applicability
41   to the full geographic extent of the three ecoregions (see Section 3.1).

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1 Despite its promise, the Panel identified a number of caveats that needed to be considered
2 when applying this methodology to other stressors:

3 **1) Natural Classifications.** The Panel concluded that the methodology can be applied to
4 other stressors where data coverage and quality are sufficient; however, the key natural
5 classification features that influence and explain variation in the stressor and taxa distributions
6 would need to be identified. For example, natural streams can vary in their background
7 concentration of dissolved oxygen as a function of stream gradient, stream morphology, and
8 stream type. These variables are often geographically independent and variation may not be
9 controlled by isolating ecoregions or other geographic constructs, but may require more reach-
10 specific data to be applied successfully. Even so, the field-based SSD methodology should be
11 transferable to such streams as long as they can be accurately classified prior to derivation and
12 application of benchmarks.

13 **2) Mode of Effect.** The field SSD methodology was readily applicable to conductivity
14 because there is a relatively direct physiological mechanism and effect between the stressor (i.e.,
15 conductivity, as a surrogate for concentrations of dissolved ions) and the occurrence of taxa. For
16 other similar stressors (e.g., dissolved oxygen, pH) a similar approach may be applicable. The
17 situation is more complex for stressors—in particular nutrients and physical habitat measures—
18 that influence the distribution of taxa indirectly. The tails of the distributions of extirpation
19 values may be particularly long and the species may persist at some sites where stressor levels
20 are suboptimal because expression of effects is moderated by other (confounding) factors. For
21 example, the effects of a specific total phosphorus level can be moderated by shading, habitat, or
22 base flow. In a stream with a total phosphorus concentration of 0.20 ppm that is a channelized
23 stream with an open canopy, many sensitive species would be eliminated. Conversely, in a
24 heavily shaded stream with a natural channel and good base flow, the same phosphorus
25 concentration would likely be associated with the occurrence of many sensitive species. Failure
26 to consider these other moderating or confounding factors could result in a benchmark that is not
27 protective for many species. Similarly, habitat stressors (e.g., bedded sediments, channel
28 modifications) can have varied effects depending on the spatial scale of impact. Widespread
29 aggradation of fine sediments or channel modifications can eliminate species/taxa from a
30 watershed. However if the sedimentation or other habitat limitations are only local, sensitive
31 species may routinely occur although at reduced abundance. In such cases, change points in
32 taxa/species abundances (e.g., Toms and Lesperance, 2003) may be the more appropriate choice
33 for a SSD statistic than an extirpation curve.

34 **3) Data Sufficiency.** The conductivity benchmark was derived from a large data set and
35 the Panel concluded that a large, robust data set would be necessary for derivation of any stressor
36 benchmark from field data. The availability of a validation data set also was identified as
37 important to the use of this method for other stressors. It would be important that the data set
38 represent the entire expected gradient of condition including stressed and non-stressed
39 (reference) sites. The size of the data set needed would increase with number of stressors (i.e.,
40 confounding factors) that can control the distribution of species/taxa in a region. This would be
41 particularly important for the assessment of causation and confounding factors analyses.

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1   **4) Tiered Aquatic Life Uses.** As States develop tiered aquatic life uses, a natural
2   consequence may be the need to develop tiered criteria for a variety of stressors. This need
3   would apply to multiple stressors and the implications or robustness of the field-based SSD
4   approach needs to be assessed. The conceptual model for the tiered use approach is provided by
5   the Biological Condition Gradient (BCG) model developed by US EPA (Davies and Jackson,
6   2006). The various tiers of the BCG are based on the presence or absence of species associated
7   with each attribute of the BCG. Thus the derivation of stressor benchmarks for tiered uses could
8   be developed by dropping or adding species that comprise the species/taxa that characterize an
9   aquatic life or BCG tier. It would be useful to address the concept of tiered aquatic life uses and
10 how this methodology might apply to conductivity and other stressors.

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3   of mountaintop coal mining: comparing biological conditions using family- and genus-
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29   for Conductivity in Central Appalachian Streams. Office of Research and Development,
30   National Center for Environmental Assessment, Washington, DC. EPA/600/R-10/023A.
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32   Derive Numeric Nutrient Criteria. Office of Water, Washington, DC. November 2010.
33   EPA-820-S-10-001.
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37   States. *Regional Environmental Change* 2(2):66-72.

SAB Draft Report dated December 28, 2010 for Quality Review - Do not Cite or Quote
This draft does not reflect consensus advice or recommendations, has not been reviewed or approved by the
chartered SAB, and does not represent EPA policy.

1   **APPENDIX A: Charge to the Panel**

2

3   **UNITED STATES ENVIRONMENTAL PROTECTION AGENCY**

4   National Center for Environmental Assessment

5   Office of Research and Development

6   June 10, 2010

7

8 **MEMORANDUM**

9

10 **SUBJECT:**   Review of (1) "The Effects of Mountaintop Mines and Valley Fills on Aquatic
11   Ecosystems of the Central Appalachian Coalfields" and (2) "A Field-based
12   Aquatic Life Benchmark for Conductivity in Central Appalachian Streams"

13

14 **FROM:**   Michael Slimak, Associate Director   */signed/*
15   National Center for Environmental Assessment
16   Office of Research and Development

17

18 **TO:**   Vanessa Vu, Director
19   Science Advisory Board Staff Office

20

21   This memorandum provides background information and specific charge questions to the
22 Science Advisory Board (SAB) in its review of two reports prepared by EPA's Office of
23 Research and Development (ORD). These reports were developed by the National Center for
24 Environmental Assessment (NCEA) upon the request of EPA's Office of Water and Regions 3,
25 4, and 5. These reports help provide scientific information to support a set of actions EPA is
26 undertaking to clarify and strengthen environmental permitting requirements for Appalachian
27 surface coal mining operations, in coordination with other federal and state regulatory agencies.

28

29 **Background**

30

31   The purpose of the report entitled "The Effects of Mountaintop Mines and Valley Fills on
32 Aquatic Ecosystems of the Central Appalachian Coalfields," is to assess the state of the science
33 on the ecological impacts of Mountaintop Mining and Valley Fill (MTM-VF) operations on
34 streams in the Central Appalachian Coal Basin. This basin covers about 12 million acres in West
35 Virginia, Kentucky, Virginia, and Tennessee. The draft EPA Report reviews literature relevant
36 to evaluating five potential consequences of MTM-VF operations: 1) impacts on headwater
37 streams; 2) impacts on downstream water quality; 3) impacts on stream ecosystems; 4) the
38 cumulative impacts of multiple mining operations; and 5) effectiveness of mining reclamation
39 and mitigation. The impacts of MTM-VF operations on cultural and aesthetic resources were not
40 included in the review. EPA used two primary sources of information for the evaluation: (1) the
41 peer reviewed, published literature and (2) the federal Programmatic Environmental Impact
42 Statement (PEIS) on Mountaintop Mining/Valley Fills in Appalachia and its associated
43 appendices prepared in draft in 2003 and finalized in 2005.
44   The second report entitled, "A Field-based Aquatic Life Benchmark for Conductivity in
45 Central Appalachian Streams," uses field data to derive an aquatic life benchmark for

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1   conductivity. This benchmark value may be applied to waters in the Appalachian Region that
2   are near neutral or mildly alkaline in their pH and where dissolved ions are dominated by salts of
3   sulfate and bicarbonate. This benchmark is intended to protect the biological integrity of waters
4   in the region. It is derived by a method modeled on EPA's standard methodology for deriving
5   water quality criteria. In particular, the methodology was adapted for the use of field data. Field
6   data were used because sufficient and appropriate laboratory data were not available and because
7   high quality field data were available to relate conductivity to effects on biotic communities.
8   This draft EPA Report provides the scientific basis for a conductivity benchmark in a specific
9   region rather than for the entire United States.
10   Both of these reports were commissioned by EPA's Office of Water (OW) and Regions
11 3, 4, and 5 in order to provide information that will assist OW and the Regions to further clarify
12 and strengthen environmental permitting requirements for Appalachian surface coal mining
13 projects, in coordination with federal and state regulatory agencies. Using the best available
14 science and applying existing legal requirements, EPA issued comprehensive guidance on April
15 1, 2010 that sets clear benchmarks for preventing significant and irreversible damage to
16 Appalachian watersheds at risk from mining activities.
17
18 **Specific Charge in Reviewing the Mountaintop Mining – Valley Fill Effects Report**
19
20   Charge Question 1: The Mountaintop Mining Assessment uses a conceptual model
21   (Figure 12 of the draft document) to formulate the problem consistent with EPA's
22   Ecological Risk Assessment Guidelines. Does the conceptual diagram include the key
23   direct and indirect ecological effects of MTM-VF? If not, please indicate the effects or
24   pathways that are missing or need additional elucidation.
25
26   Charge Question 2: This report relied solely on peer-reviewed, published literature and
27   the 2005 Final Programmatic Environmental Impact Assessment on Mountaintop
28   Mining/Valley Fills. Does this assessment report include the most relevant peer-
29   reviewed, published literature on this topic? If not, please indicate which references are
30   missing.
31
32   Charge Question 3: Valley fills result in the direct loss of headwater streams. Has the
33   review appropriately characterized the ecological effects of the loss of headwater
34   streams?
35
36   Charge Question 4: In addition to impacts on headwater streams, mining and valley fills
37   affect downstream water quality and stream biota. Does the report effectively
38   characterize the causal linkages between MTM-VF downstream water quality and effects
39   on stream biota?
40
41   Charge Question 5: The published literature is sparse regarding the cumulative
42   ecological impacts of filling headwater streams with mining waste (spoil). Does the
43   review accurately describe the state of knowledge on cumulative ecological impacts of
44   MTM-VF? If not, how can it be improved?
45

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chartered SAB, and does not represent EPA policy.

1   Charge Question 6: The Surface Mining Control and Reclamation Act and its
2   implementing regulations set requirements for ensuring the restoration of lands disturbed
3   by mining through restoring topography, providing for post-mining land use, requiring
4   re-vegetation, and ensuring compliance with the Clean Water Act. Does the review
5   appropriately characterize the effectiveness of currently employed restoration methods?
6
7   **Specific Charge in Reviewing the Conductivity Benchmark Report**
8
9   Charge Question 1: The data sets used to derive a conductivity benchmark (described in
10 Section 2 of this report) were developed primarily by two central Appalachian states
11 (WV and KY). Please comment on the adequacy of these data and their use in developing
12 a conductivity benchmark.
13
14 Charge Question 2: The derivation of a benchmark value for conductivity was adapted
15 from EPA's methods for deriving water quality criteria. The water quality criteria
16 methodology relies on a lab-based procedure, whereas this report uses a field-based
17 approach. Has the report adapted the water quality criteria methodology to derive a water
18 quality advisory for conductivity using field data in a way that is clear, transparent and
19 reasonable?
20
21 Charge Question 3: Appendix A of the report describes the process used to establish a
22 causal relationship between the extirpation of invertebrate genera and levels of
23 conductivity. Has the report effectively made the case for a causal relationship between
24 species extirpation and high levels of conductivity due to surface coal mining activities?
25
26 Charge Question 4: In using field data, other variables and factors have to be accounted
27 for in determining causal relationships. Appendix B of the report describes the
28 techniques for dealing with confounding factors. Does the report effectively consider
29 other factors that may confound the relationship between conductivity and extirpation of
30 invertebrates? If not, how can the analysis be improved?
31
32 Charge Question 5: Uncertainty values were analyzed using a boot-strapped statistical
33 approach. Does the SAB agree with the approach used to evaluate uncertainty in the
34 benchmark value? If not, how can the uncertainty analysis be improved?
35
36 Charge Question 6: The field-based method results in a benchmark value that the report
37 authors believe is comparable to a chronic endpoint. Does the Panel agree that the
38 benchmark derived using this method provides for a degree of protection comparable to
39 the chronic endpoint of conventional ambient water quality criteria?
40
41 Charge Question 7: As described, the conductivity benchmark is derived using central
42 Appalachian field data and has been validated within ecoregions 68, 69, and 70. Under
43 what conditions does the SAB believe this method would be transferable to developing a
44 conductivity benchmark for other regions of the United States whose streams have a
45 different ionic signature?
46

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chartered SAB, and does not represent EPA policy.

1   Charge Question 8: The amount and quality of field data available from the states and the
2   federal government have substantially increased throughout the years. In addition, the
3   computing power available to analysts continues to increase. Given these enhancements
4   in data availability and quality and computing power, does the Panel feel it feasible and
5   advisable to apply this field-based method to other pollutants? What issues should be
6   considered when applying the method to other pollutants?
7
8
9   **Background Reading Materials**
10
11   The following documents are accessible via the hyperlinks provided below. These
12 documents provide important background information from scientific, regulatory, and policy
13 perspectives on mountaintop mining and valley fills and are recommended reading for the SAB
14 Panel members.
15
16   1. Final Programmatic Environmental Impact Statement on Mountaintop Mining/Valley
17   Fills in Appalachia – 2005
18   htttp://www.epa.gov/region3/mtntop/eis2005.htm)
19   2. April 1, 2010 Guidance Memorandum on Appalachian Surface Coal Mining
20   http://www.epa.gov/owow/wetlands/guidance/pdf/appalachian_mtntop_mining_d
21   etailed.pdf.
22

Matthew Klasen/DC/USEPA/US

01/05/2011 05:28 PM

To   Gregory Peck, Kevin Minoli

cc   MichaelG Lee

bcc

Subject   Fw: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Here's the most recent from Mike on the Rahall letter. Based on the fact that there are some substantive things here, and that it would be terrible to take Stef off Spruce for even a minute, I think next week makes the most sense.

OWM and R3 are OK with this (Ev was going to send a small change), but getting up to R3 management is probably the limiting factor.

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/05/2011 05:26 PM -----

From:	MichaelG Lee/DC/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Cc:	Js Wilson/DC/USEPA/US@EPA
Date:	01/05/2011 03:58 PM
Subject:	Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Matt,
Here are my quick edits/comments. Let me know if you find out that we've got substantially more time on this -- I may run it past some folk in my shop with more specialized knowledge on a topic or two.

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-05 Draft Rahall Response on 402 - Clean.doc

Mike

Michael G. Lee
Office of General Counsel
(202) 564-5486

Matthew Klasen   Mike, Stef, and Ev **(b) (5)**   01/05/2011 11:44:30 AM

From:	Matthew Klasen/DC/USEPA/US
To:	MichaelG Lee/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA
Date:	01/05/2011 11:44 AM
Subject:	Re: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Mike, Stef, and Ev:

(b) (5)

.

Anyway, just a heads up. Mike and Ev, if you could take a look at this soon, that would be great. Stef, I know you have nothing else you're working on, but you may also have to look at this fairly quickly. We can ask Bob and folks at the 1:00.

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Matthew Klasen	Hi everyone, As promised on yesterday mornin...	01/05/2011 11:03:17 AM

From:	Matthew Klasen/DC/USEPA/US
To:	Chris Thomas/R4/USEPA/US@EPA, Deborah Nagle/DC/USEPA/US@EPA, Denis Borum/DC/USEPA/US@EPA, Diane Jones-Coleman/DC/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Js Wilson/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Linda Boornazian/DC/USEPA/US@EPA, Marcus Zobrist/DC/USEPA/US@EPA, MichaelG Lee/DC/USEPA/US@EPA, Sharmin Syed/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Tom Laverty/DC/USEPA/US@EPA
Cc:	Bob Sussman/DC/USEPA/US@EPA, Nancy Stoner/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA
Date:	01/05/2011 11:03 AM
Subject:	Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Hi everyone,

As promised on yesterday morning's mining call, attached is an updated draft response letter to Congressman Rahall regarding EPA 402 actions in WV (not on Spruce). I've included both a clean version and a Track Changes version.

I've taken the original draft that Evelyn put together back in December, added the mid-December comments from Mark in R4, incorporated preliminary edits/comments from Mike Lee in OGC, and made some additional edits (like moving the specific question responses to the end of the letter rather than in the middle).

I'd be happy to continue to be the compiler of edits to this, or Evelyn or others in R3 could take that on. Let me know what works best.

Comments by noon tomorrow I think would be great, in prep for sending this out either later this week or next week (probably the latter, given Spruce).

Thanks,
Matt

[attachment "2011-01-05 Draft Rahall Response on 402 - Track Changes.docx" deleted by Matthew Klasen/DC/USEPA/US] [attachment "2011-01-05 Draft Rahall Response on 402 - Clean.docx" deleted by Matthew Klasen/DC/USEPA/US]

Matt Klasen

U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

		To	stefshamet
Matthew Klasen/DC/USEPA/US		cc	
01/05/2011 05:44 PM		bcc	
		Subject	Fw: 114-240

Here ya go.

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229
----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/05/2011 05:43 PM -----

From:	Stefania Shamet/R3/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Date:	01/05/2011 04:00 PM
Subject:	114-240

(b) (5)

He's going to revise those tonight and will send in the am.

ATTACHMENT REDACTED – DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responsessds.docx

Matthew Klasen/DC/USEPA/US	To	Christopher Hunter	
01/05/2011 05:57 PM	cc		
	bcc		
	Subject	Fw: 114-240	

We're on track with these; Stef has gone through the whole remaining section that we haven't yet given Kevin.

Kevin will be occupied with mitigation tonight, and we'll get him 114-240 mid-morning tomorrow. Then, it's writing responses to the 5 questions we don't yet have answers to, fixing any Se ones, adding Denise's comments, and incorporating Kevin's edits.

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/05/2011 05:56 PM -----

From:	Stefania Shamet/R3/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Date:	01/05/2011 04:00 PM
Subject:	114-240

(b) (5)

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ATTACHMENT REDACTED - DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responsessds.docx

Matthew
Klasen/DC/USEPA/US
01/05/2011 07:19 PM

To "Denis Borum"

cc

bcc

Subject Fw: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

FYI -- again, apologies for missing you on the list (especially after mentioning "OCIR" in the message).

Matt Klasen
U.S. Environmental Protection Agency
Office of Water
(202) 566-0780
Cell (202) 380-7229
    Matthew Klasen

  ----- Original Message -----
    From: Matthew Klasen
    Sent: 01/05/2011 06:52 PM EST
    To: Evelyn MacKnight
    Cc: Stefania Shamet; MichaelG Lee; Kevin Minoli; Gregory Peck; Js Wilson; Tom Laverty; Deborah Nagle; Jim Giattina; Mark Nuhfer
    Subject: Fw: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Hi Evelyn,

See below for some edits from Mike Lee on the draft response to Rahall on 402 issues.

(b) (5)

Can you take a look at Mike's edits/comments, make sure you're comfortable with these suggestions (they look helpful to me), and make sure Jon, Bill, and Shawn are aware? (I think OCIR may also be contacting Shawn et al.)

OWM: Note Mike's concerns regarding PQR checklists, which may be something you should weigh in on.

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/05/2011 06:43 PM -----

From:	MichaelG Lee/DC/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Cc:	Js Wilson/DC/USEPA/US@EPA
Date:	01/05/2011 03:58 PM
Subject:	Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Matt,
Here are my quick edits/comments. Let me know if you find out that we've got substantially more time on

this -- I may run it past some folk in my shop with more specialized knowledge on a topic or two.

 ATTACHMENT REDACTED - DELIBERATIVE

2011-01-05 Draft Rahall Response on 402 - Clean - Mike Lee.doc

Mike

Michael G. Lee
Office of General Counsel
(202) 564-5486

| Matthew Klasen | Mike, Stef, and Ev: (b) (5) | 01/05/2011 11:44:30 AM |

From:	Matthew Klasen/DC/USEPA/US
To:	MichaelG Lee/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA
Date:	01/05/2011 11:44 AM
Subject:	Re: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Mike, Stef, and Ev:

(b) (5)

Anyway, just a heads up. Mike and Ev, if you could take a look at this soon, that would be great. Stef, I know you have nothing else you're working on, but you may also have to look at this fairly quickly. We can ask Bob and folks at the 1:00.

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

| Matthew Klasen | Hi everyone, As promised on yesterday mornin... | 01/05/2011 11:03:17 AM |

From:	Matthew Klasen/DC/USEPA/US
To:	Chris Thomas/R4/USEPA/US@EPA, Deborah Nagle/DC/USEPA/US@EPA, Denis Borum/DC/USEPA/US@EPA, Diane Jones-Coleman/DC/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Js Wilson/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Linda Boornazian/DC/USEPA/US@EPA, Marcus Zobrist/DC/USEPA/US@EPA, MichaelG Lee/DC/USEPA/US@EPA, Sharmin Syed/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Tom Laverty/DC/USEPA/US@EPA
Cc:	Bob Sussman/DC/USEPA/US@EPA, Nancy Stoner/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA
Date:	01/05/2011 11:03 AM
Subject:	Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Hi everyone,

As promised on yesterday morning's mining call, attached is an updated draft response letter to Congressman Rahall regarding EPA 402 actions in WV (not on Spruce). I've included both a clean version and a Track Changes version.

I've taken the original draft that Evelyn put together back in December, added the mid-December comments from Mark in R4, incorporated preliminary edits/comments from Mike Lee in OGC, and made some additional edits (like moving the specific question responses to the end of the letter rather than in the middle).

I'd be happy to continue to be the compiler of edits to this, or Evelyn or others in R3 could take that on. Let me know what works best.

Comments by noon tomorrow I think would be great, in prep for sending this out either later this week or next week (probably the latter, given Spruce).

Thanks,
Matt

[attachment "2011-01-05 Draft Rahall Response on 402 - Track Changes.docx" deleted by Matthew Klasen/DC/USEPA/US] [attachment "2011-01-05 Draft Rahall Response on 402 - Clean.docx" deleted by Matthew Klasen/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Greg Pond/R3/USEPA/US   To   Margaret Passmore

01/05/2011 07:35 PM   cc   John Forren, Matthew Klasen, Stefania Shamet

                                  bcc

                         Subject   Re: 125A

Stef, please see my edits and additions for 124A and 125A. I queried data from PR and OH and put into a table. Hope this clears it up.

Greg

ATTACHMENT REDACTED - DELIBERATIVE

124Aand 125A.doc

Greg Pond
Office of Monitoring and Assessment
U.S. EPA Region 3
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
(p) 304-234-0243
(f) 304-234-0260
pond.greg@epa.gov
Website: http://epa.gov/reg3esd1/3ea50.htm

Margaret Passmore   (b) (5)   01/05/2011 07:46:17 AM

From: Margaret Passmore/R3/USEPA/US
To: Stefania Shamet/R3/USEPA/US@EPA
Cc: Greg Pond/R3/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA, Matthew
           Klasen/DC/USEPA/US@EPA
Date: 01/05/2011 07:46 AM
Subject: Re: 125A

(b) (5)

Margaret Passmore
Freshwater Biology Team
Office of Monitoring and Assessment (3EA50)
Environmental Assessment and Innovation Division
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1060 Chapline Street, Suite 303

Wheeling, WV 26003-2995
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passmore.margaret@epa.gov

Visit our website at http://epa.gov/reg3esd1/3ea50.htm

| Stefania Shamet | (b) (5) | 01/05/2011 05:17:18 AM |

From: Stefania Shamet/R3/USEPA/US
To: Greg Pond/R3/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA
Cc: Matthew Klasen/DC/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA
Date: 01/05/2011 05:17 AM
Subject: 125A

(b) (5)

David Rider/R3/USEPA/US   To   David Kargbo
01/06/2011 08:39 AM   cc
                                     bcc
                              Subject   Selenium - Exhibits and Tech Eval Doc--Mingo Logan
                                        Comments on RD Nov 2010.pdf

Dave,

Here is the electronic path to the volume on your desk.

L:\Share\Mountaintop\Exhibits and Tech Eval Doc--Mingo Logan Comments on RD Nov 2010.pdf

Dave

Julia McCarthy/R8/USEPA/US

01/06/2011 11:16 AM

To Christopher Hunter

cc

bcc

Subject Re: Revised Executive Summary

One very minor edit...

[W icon]   ATTACHMENT REDACTED – DELIBERATIVE

Revised Spruce 404c Executive Summary_jmm.doc

Julia McCarthy
on detail to USEPA Headquarters
Office of Wetlands, Oceans and Watersheds
(202) 566-1660
mccarthy.julia@epa.gov

A land ethic, then, reflects the existence of an ecological conscience, and this in turn reflects a connection of individual responsibility for the health of the land. Health is the capacity of the land for self-renewal. Conservation is our effort to understand and preserve this capacity. ~Aldo Leopold

---

| Christopher Hunter | Dave and Brian, attached is the revised executi... | 01/06/2011 11:03:12 AM |

From: Christopher Hunter/DC/USEPA/US
To: Brian Frazer/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA
Cc: Julia McCarthy/R8/USEPA/US@EPA
Date: 01/06/2011 11:03 AM
Subject: Revised Executive Summary

Dave and Brian,
attached is the revised executive summary, as requested by Nancy. This version includes your comments. Please review and forward to Denise.

Thanks,
Chris
[attachment "Revised Spruce 404c Executive Summary.doc" deleted by Julia McCarthy/R8/USEPA/US]

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Ross Geredien/DC/USEPA/US

01/06/2011 11:19 AM

To Julia McCarthy

cc Christopher Hunter, Marcel Tchaou

bcc

Subject Re: 303 d

Chris,

     Here is the corrected paragraph for p. 73. (b) (5)

ATTACHMENT REDACTED - DELIBERATIVE

Coal River Impaired Streams p. 73.docx

Ross Geredien
ORISE Fellow
EPA Office of Wetlands, Oceans, and Watersheds
202-566-1466
Geredien.ross(AT)epa.gov

| Julia McCarthy | http://www.dep.wv.gov/WWE/watershed/IR/Doc... | 01/06/2011 10:51:18 AM |

From: Julia McCarthy/R8/USEPA/US
To: Ross Geredien/DC/USEPA/US@EPA
Date: 01/06/2011 10:51 AM
Subject: 303 d

http://www.dep.wv.gov/WWE/watershed/IR/Documents/IR_2010_Documents/WV_2010_IR_Narrative_and_Supplements_FINAL_20101109.pdf

Coal River Watershed is on page 66

Julia McCarthy
on detail to USEPA Headquarters
Office of Wetlands, Oceans and Watersheds
(202) 566-1660
mccarthy.julia@epa.gov

A land ethic, then, reflects the existence of an ecological conscience, and this in turn reflects a connection of individual responsibility for the health of the land. Health is the capacity of the land for self-renewal. Conservation is our effort to understand and preserve this capacity. ~Aldo Leopold

To Matthew Klasen

cc Carrie Traver, Christopher Hunter, Greg Pond, Stefania Shamet

bcc

Subject Re: Fw: Spruce References list

Hi Everyone,
This is the current version that I am working on now updating it.

ATTACHMENT REDACTED - DELIBERATIVE

Appendix 7 FD Marcel version 1-06-2011.doc

****
Marcel K. Tchaou, Ph.D., P.E., P.H.
Environmental Engineer
Wetlands & Aquatic Resources Regulatory Branch
Office of Wetlands, Oceans and Watersheds
U.S. EPA
1200 Pennsylvania Avenue, NW (MC 4502T)
Washington, DC 20460
202-566-1904

Matthew Klasen	Chris, Marcel, and Carrie: See Greg's note belo...	01/06/2011 11:16:24 AM

From:	Matthew Klasen/DC/USEPA/US
To:	Marcel Tchaou/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Carrie Traver/R3/USEPA/US@EPA
Cc:	Greg Pond/R3/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/06/2011 11:16 AM
Subject:	Fw: Spruce References list

Chris, Marcel, and Carrie:

See Greg's note below. Can someone send Greg the most recent reference list?

This begs the question of what the most effective process should be for both verifying the reference list itself, and ensuring that all our responses (FD, PD comments, RD comments) don't cite new things and cite the right things (including things that are actually in the list).

I'm interested in hearing suggestions on what seems best to folks. We're getting close to the point where a significant portion of the RD responses are nearly done, following OGC review and resolution of OGC comments. I'd be willing to start sending out chunks of the compiled OGC-reviewed RD responses to folks to start checking references, which is something that needs to be done but that I'm probably not most qualified to do.

That said, for version control, Chris and I still need to maintain the compiler roles throughout this process.

Thoughts on process?

Thanks.
Matt
.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

From:	Greg Pond/R3/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Date:	01/06/2011 11:07 AM
Subject:	Spruce References list

Matt, **(b) (5)** Can you send
me the "list"? When I go the ESC, there are all the references, but no list.

Thanks,

Greg

Greg Pond
Office of Monitoring and Assessment
U.S. EPA Region 3
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
(p) 304-234-0243
(f) 304-234-0260
pond.greg@epa.gov
Website: http://epa.gov/reg3esd1/3ea50.htm

David Evans/DC/USEPA/US

01/06/2011 12:59 PM

To Denise Keehner

cc Benita Best-Wong, Jim Pendergast, Brian Frazer, Lynda Hall, Christopher Hunter, Julia McCarthy

bcc

Subject Revised Executive Summary

Denise,

Attached below is a comprehensively revised/substantively expanded draft of the Spruce Veto Executive Summary. All credit to Julia and Chris; Brian and I have reviewed and fully endorse this version.

Look forward to your feedback, questions, comments.

Dave

David Evans, Director
Wetlands Division
Office of Wetlands, Oceans and Watersheds
(202) 566-0535

----- Forwarded by David Evans/DC/USEPA/US on 01/06/2011 12:56 PM -----

From:	Christopher Hunter/DC/USEPA/US
To:	Brian Frazer/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA
Cc:	Julia McCarthy/R8/USEPA/US@EPA
Date:	01/06/2011 11:03 AM
Subject:	Revised Executive Summary

Dave and Brian,
attached is the revised executive summary, as requested by Nancy. This version includes your comments. Please review and forward to Denise.

Thanks,
Chris

ATTACHMENT REDACTED – DELIBERATIVE

Revised Spruce 404c Executive Summary.doc

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

**Stefania
Shamet/R3/USEPA/US**
01/06/2011 01:58 PM

To   Matthew Klasen

cc

bcc

Subject   140A-180A

Except for 146,A, 150A, 154A, 165A (Remember that I always send the whole doc to avoid messing up numbering. done through 180A)

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responsessds.docx

Matthew Klasen/DC/USEPA/US
01/06/2011 02:05 AM

To Matthew Klasen

cc

bcc

Subject Comments

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780

cell (202) 380-7229 ⬜ - 2011-01-06 Compiled H&W RD Comment Responses.docx ⬜ -
2011-01-06 Compiled WVDEP RD Comment Responses.doc

ATTACHMENTS REDACTED – DELIBERATIVE

Christopher Hunter/DC/USEPA/US

01/06/2011 03:01 PM

To   Gregory Peck

cc   Brian Frazer

bcc

Subject   Spruce short narrative draft

ATTACHMENT REDACTED - DELIBERATIVE

Spruce narrative 2-pager.doc

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

There are actually 3 spreadsheets with raw data that pertain to the golden algae section. I separated them because they came from different places, but it might be better just to lump them together.

The three are:

Pennsylvania Department of Environmental Protection. (PADEP) (unpublished). Golden algae data,"Algae.xls."CONSOL & PADEP 2009 compilation by PADEP from PADEP and CONSOL data.

USEPA (unpublished) Golden algae data, "Bailey_P parvum summary" compiled by USEPA from 2010 CONSOL data.

Hambright, K. D. (unpublished). Golden algae data results, "WV-PA-Summary-qPCR results.xls. 2009 samples collected by WVDEP, PADEP and USEPA and sent to Dr. David Hambright's laboratory.

Carrie Traver
USEPA Region 3
Office of Environmental Programs
1650 Arch Street - 3EA30
Philadelphia, PA 19103
215-814-2772
traver.carrie@epa.gov

Louis Reynolds	This citation is to data supplied by Dr. Hambrigh...	01/06/2011 02:46:25 PM

From:	Louis Reynolds/R3/USEPA/US
To:	Carrie Traver/R3/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, Marcel Tchaou/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA
Date:	01/06/2011 02:46 PM
Subject:	Re: Check this

This citation is to data supplied by Dr. Hambright to USEPA and WVDEP. This data was cited in response to comments to the RD.

There is also a cite on page 66 of the FD (in the golden algae section):

2. *High TDS:* The lower TDS limits for the growth of *P. parvum* appears to be ~500 mg/l TDS, or ~700µS/cm conductivity for the ion mixtures typical of alkaline mine drainage (Hambright 2010). Recent data indicate that growth of *P. parvum* increases 200-300% when conductivity increases from 500 µS/cm to 1000 ìS/cm (<mark>unpublished data, WVDEP, 2010</mark>, Hambright 2010). The waters draining the nearby Dal-Tex Mine operation have conductivity levels greater than these values. Many of the sampling sites on the main stem of Spruce Fork, Pond Fork and the Little Coal River also have conductivity levels exceeding these endpoints. Other waters of

concern near the Spruce No. 1 Mine include the Little Coal River and West Fork/Pond Fork. As described in SectionV.D.1.b., construction of valley fills and other discharges authorized by DA Permit No 199800436-3 (Section 10: Coal River) into Pigeonroost Branch and Oldhouse Branch is expected to increase levels of TDS/conductivity in Spruce Fork, thus creating conditions more favorable to *P. parvum* .

Hambright 2010 is a cite to his report. That must stay.

The highlighted cite should be removed from the text, because it is redundant.

If you are still confused - call me

Lou Reynolds
USEPA Region III
Freshwater Biology Team
1060 Chapline St. Ste. 303
Wheeling, WV 26003-2995
P 304-234-0244
F 304-234-0260

Carrie Traver	I'm not sure. That is a question for Lou Reynold...	01/06/2011 01:55:14 PM

From:	Carrie Traver/R3/USEPA/US
To:	Marcel Tchaou/DC/USEPA/US@EPA, Louis Reynolds/R3/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA
Date:	01/06/2011 01:55 PM
Subject:	Re: Check this

I'm not sure. That is a question for Lou Reynolds. I believe he sent the data because he used it for the section on golden algae.

Carrie Traver
USEPA Region 3
Office of Environmental Programs
1650 Arch Street - 3EA30
Philadelphia, PA 19103
215-814-2772
traver.carrie@epa.gov

Marcel Tchaou	Chris and Carrie, Does it make sense to use thi...	01/06/2011 01:45:15 PM

From:	Marcel Tchaou/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA, Carrie Traver/R3/USEPA/US@EPA
Cc:	Matthew Klasen/DC/USEPA/US@EPA
Date:	01/06/2011 01:45 PM
Subject:	Check this

Chris and Carrie,

Does it make sense to use this reference?

Hambright, K. D. (unpublished). Golden algae data results, "WV-PA-Summary-qPCR results.xls. 2009 samples collected by WVDEP, PADEP and USEPA and sent to Dr. David Hambright's laboratory.

****
Marcel K. Tchaou, Ph.D., P.E., P.H.
Environmental Engineer
Wetlands & Aquatic Resources Regulatory Branch
Office of Wetlands, Oceans and Watersheds
U.S. EPA
1200 Pennsylvania Avenue, NW (MC 4502T)
Washington, DC 20460
202-566-1904

Marcel Tchaou/DC/USEPA/US	To	Matthew Klasen
01/06/2011 03:28 PM	cc	Carrie Traver, Christopher Hunter, Greg Pond, Stefania Shamet
	bcc	
	Subject	Re: Fw: Spruce References list

Folks,
This is latest version of the Reference list as of 3:27 PM on 01/06/10

ATTACHMENT REDACTED - DELIBERATIVE

Appendix 7 FD Marcel version 1-06-2011.doc

****
Marcel K. Tchaou, Ph.D., P.E., P.H.
Environmental Engineer
Wetlands & Aquatic Resources Regulatory Branch
Office of Wetlands, Oceans and Watersheds
U.S. EPA
1200 Pennsylvania Avenue, NW (MC 4502T)
Washington, DC 20460
202-566-1904

| Matthew Klasen | Chris, Marcel, and Carrie: See Greg's note belo... | 01/06/2011 11:16:24 AM |

From:	Matthew Klasen/DC/USEPA/US
To:	Marcel Tchaou/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Carrie Traver/R3/USEPA/US@EPA
Cc:	Greg Pond/R3/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/06/2011 11:16 AM
Subject:	Fw: Spruce References list

Chris, Marcel, and Carrie:

See Greg's note below. Can someone send Greg the most recent reference list?

This begs the question of what the most effective process should be for both verifying the reference list itself, and ensuring that all our responses (FD, PD comments, RD comments) don't cite new things and cite the right things (including things that are actually in the list).

I'm interested in hearing suggestions on what seems best to folks. We're getting close to the point where a significant portion of the RD responses are nearly done, following OGC review and resolution of OGC comments. I'd be willing to start sending out chunks of the compiled OGC-reviewed RD responses to folks to start checking references, which is something that needs to be done but that I'm probably not most qualified to do.

That said, for version control, Chris and I still need to maintain the compiler roles throughout this process.

Thoughts on process?

Thanks.
Matt
.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

From:	Greg Pond/R3/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Date:	01/06/2011 11:07 AM
Subject:	Spruce References list

Matt, (b) (5)   Can you send
me the "list"? When I go the ESC, there are all the references, but no list.

Thanks,

Greg

Greg Pond
Office of Monitoring and Assessment
U.S. EPA Region 3
1060 Chapline Street, Suite 303
Wheeling, WV 26003-2995
(p) 304-234-0243
(f) 304-234-0260
pond.greg@epa.gov
Website: http://epa.gov/reg3esd1/3ea50.htm

Stefania Shamet/R3/USEPA/US	To	Evelyn MacKnight
01/06/2011 03:28 PM	cc	Amy Caprio, Chris Thomas, Deborah Nagle, Gregory Peck, Jessica Greathouse, Jim Giattina, Jon Capacasa, Js Wilson, Kevin Minoli, Linda Boornazian, "Philip Mancusi-Ungaro", Marcus Zobrist, Mark Nuhfer, Matthew Klasen, "Stan Meiburg", MichaelG Lee, "Paul Schwartz", Tom Laverty, William Early, Shawn Garvin, Michael DAndrea, Catherine Libertz
	bcc	
	Subject	Re: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

(b) (5) ███

ATTACHMENT REDACTED - DELIBERATIVE

Rahall 1611 draft.doc

Evelyn MacKnight	FYI. **(b) (5)** ████████████████████	01/06/2011 01:25:04 PM

From:	Evelyn MacKnight/R3/USEPA/US
To:	Jim Giattina/R4/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Jessica Greathouse/R3/USEPA/US@EPA, William Early/R3/USEPA/US
Cc:	Deborah Nagle/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Js Wilson/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, "Philip Mancusi-Ungaro" <Mancusi-Ungaro.Philip@epamail.epa.gov>, Mark Nuhfer/R4/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, "Stan Meiburg" <Meiburg.Stan@epamail.epa.gov>, MichaelG Lee/DC/USEPA/US@EPA, "Paul Schwartz" <Schwartz.Paul@epamail.epa.gov>, Stefania Shamet/R3/USEPA/US@EPA, Tom Laverty/DC/USEPA/US@EPA, Linda Boornazian/DC/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Chris Thomas/R4/USEPA/US@EPA, Mark Nuhfer/R4/USEPA/US@EPA, Amy Caprio/R3/USEPA/US@EPA, Marcus Zobrist/DC/USEPA/US@EPA
Date:	01/06/2011 01:25 PM
Subject:	Re: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

FYI. **(b) (5)** ███
███
██████████████████████ Any questions, please let me know.

[attachment "2011-01-06 Draft Rahall Response on 402 Emacknight.doc" deleted by Stefania Shamet/R3/USEPA/US]

Evelyn S. MacKnight
Chief, NPDES Permits Branch (3WP41)
Water Protection Division
Phone: 215-814-5717
Fax: 215-814-2301
email: macknight.evelyn@epa.gov

Matthew Klasen/DC/USEPA/US	To	Gregory Peck, MichaelG Lee
01/06/2011 03:31 PM	cc	Kevin Minoli, Karyn Wendelowski
	bcc	
	Subject	Fw: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229
----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/06/2011 03:29 PM -----

From:	Stefania Shamet/R3/USEPA/US
To:	Evelyn MacKnight/R3/USEPA/US@EPA
Cc:	Amy Caprio/R3/USEPA/US@EPA, Chris Thomas/R4/USEPA/US@EPA, Deborah Nagle/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Jessica Greathouse/R3/USEPA/US@EPA, Jim Giattina/R4/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Js Wilson/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Linda Boornazian/DC/USEPA/US@EPA, "Philip Mancusi-Ungaro" <Mancusi-Ungaro.Philip@epamail.epa.gov>, Marcus Zobrist/DC/USEPA/US@EPA, Mark Nuhfer/R4/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, "Stan Meiburg" <Meiburg.Stan@epamail.epa.gov>, MichaelG Lee/DC/USEPA/US@EPA, "Paul Schwartz" <Schwartz.Paul@epamail.epa.gov>, Tom Laverty/DC/USEPA/US@EPA, William Early/R3/USEPA/US, Shawn Garvin/R3/USEPA/US@EPA, Michael DAndrea/R3/USEPA/US@EPA, Catherine Libertz/R3/USEPA/US@EPA
Date:	01/06/2011 03:28 PM
Subject:	Re: Updated draft Rahall response re: EPA 402 actions in WV (proposed for R3 signature)

Read this v. quickly. A couple of minor revisions. I changed how the April 1 guidance was characterized to match the latest language I have from OGC. I also added the concept that permitting authority passes when the times expire if the State hasn't submitted a revised draft permit that satisfies the objection.

ATTACHMENT REDACTED - DELIBERATIVE

Rahall 1611 draft.doc

Evelyn MacKnight	FYI. Here is the latest version. I have incorpora...	01/06/2011 01:25:04 PM

From:	Evelyn MacKnight/R3/USEPA/US
To:	Jim Giattina/R4/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Jessica Greathouse/R3/USEPA/US@EPA, William Early/R3/USEPA/US
Cc:	Deborah Nagle/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Js Wilson/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, "Philip Mancusi-Ungaro" <Mancusi-Ungaro.Philip@epamail.epa.gov>, Mark Nuhfer/R4/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, "Stan Meiburg" <Meiburg.Stan@epamail.epa.gov>, MichaelG Lee/DC/USEPA/US@EPA, "Paul Schwartz" <Schwartz.Paul@epamail.epa.gov>, Stefania Shamet/R3/USEPA/US@EPA, Tom Laverty/DC/USEPA/US@EPA, Linda Boornazian/DC/USEPA/US@EPA, Jon Capacasa/R3/USEPA/US@EPA, Chris Thomas/R4/USEPA/US@EPA, Mark Nuhfer/R4/USEPA/US@EPA, Amy Caprio/R3/USEPA/US@EPA, Marcus Zobrist/DC/USEPA/US@EPA

FYI. Here is the latest version. I have incorporated info regarding authority passing to EPA post permit objection and a reference to the guidance per the latest comments. I wanted to get this out to folks again for review. Bill and Jessica, This has been reviewed extensively in HQ's, but you may have not seen it yet, so I'm passing this along. Any questions, please let me know.

[attachment "2011-01-06 Draft Rahall Response on 402 Emacknight.doc" deleted by Stefania Shamet/R3/USEPA/US]

Evelyn S. MacKnight
Chief, NPDES Permits Branch (3WP41)
Water Protection Division
Phone: 215-814-5717
Fax: 215-814-2301
email: macknight.evelyn@epa.gov

Evelyn MacKnight/R3/USEPA/US

01/06/2011 03:52 PM

To Matthew Klasen

cc Stefania Shamet, Rhonda Purnell, Shawn Garvin, Janice Donlon, Amy Caprio, Jessica Greathouse, Jon Capacasa, Linda Boornazian

bcc

Subject Re: Boilerplate on conductivity benchmark language for response to comments

(b) (5) ███████████████████████████████████

ATTACHMENT REDACTED – DELIBERATIVE

Rahall 1611 v2 draft.doc

| Matthew Klasen | (b) (5) ████████████████ | 01/06/2011 03:39:20 PM |

From: Matthew Klasen/DC/USEPA/US
To: Stefania Shamet/R3/USEPA/US@EPA, Evelyn MacKnight/R3/USEPA/US@EPA
Date: 01/06/2011 03:39 PM
Subject: Re: Boilerplate on conductivity benchmark language for response to comments

(b) (5) ███████████████████████████████████

mk

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

| Stefania Shamet | (b) (5) ████████████████ | 01/06/2011 03:16:21 PM |

From: Stefania Shamet/R3/USEPA/US
To: Matthew Klasen/DC/USEPA/US@EPA
Cc: Brian Frazer/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Kevin Minoli/DC/USEPA/US@EPA, Michael Slimak/DC/USEPA/US@EPA, Greg Pond/R3/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA
Date: 01/06/2011 03:16 PM
Subject: Re: Boilerplate on conductivity benchmark language for response to comments

(b) (5) ███████████████████████████████████

| Matthew Klasen | Hi everyone, Kevin's nearly to the section that b... | 01/06/2011 03:10:59 PM |

From: Matthew Klasen/DC/USEPA/US
To: Kevin Minoli/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Brian Frazer/DC/USEPA/US@EPA
Cc: Michael Slimak/DC/USEPA/US@EPA
Date: 01/06/2011 03:10 PM

Hi everyone,

Kevin's nearly to the section that begins to raise Hunton & Williams comments on the conductivity benchmark report (which they inappropriately characterize as "EPA's conductivity limit").

Like Kevin has done for mitigation and WQS -- and consistent with this morning's discussion -- I think we need a boilerplate statement that can apply to all of these questions (beginning with #140A).

Here's a proposal:

(b) (5)

Mike: I'm including you on this as a FYI; give me a call if you'd like me to clarify this. Let me know if the characterizations of the SAB's draft conclusions don't seem right.

Thanks,
Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Jaclyn McIlwain/R3/USEPA/US	To	Evelyn MacKnight
01/06/2011 04:12 PM	cc	
	bcc	
	Subject	Re: Packet for Linda (and me)

A copy of the graphs:

ATTACHMENT REDACTED - DELIBERATIVE

Summary of Mining Reviews LAST UPDATED Nov 3 2010.xls

I need to update the title of this. Furthermore, there are several worksheets that look incoherent because I only used them to organize data. The tab titled "Graphs" is the page that includes the tables I used, as well as all the graphs in one spot.

Jaclyn McIlwain
NPDES Permits Branch (3WP41)
Water Protection Division
U.S. EPA Region III
1650 Arch Street
Philadelphia, PA 19103

Ph: 215.814.2713
Fax: 215.814.2302
mcilwain.jaclyn@epa.gov

| Evelyn MacKnight | Jaclyn, I need your help pulling together some in... | 01/06/2011 09:36:08 AM |

From:	Evelyn MacKnight/R3/USEPA/US
To:	Jaclyn Mcilwain/R3/USEPA/US@EPA
Cc:	Bette Conway/R3/USEPA/US@EPA, Brian Trulear/R3/USEPA/US@EPA
Date:	01/06/2011 09:36 AM
Subject:	Packet for Linda (and me)

Jaclyn, I need your help pulling together some info, please obtain/print out two sets of at least this info.

WV Narrative Guidance and Justification
VA Narrative Guidance

Ison Rock Ridge Specific Objection

Any WV Specific Objections

The summary spreadsheet of permits received.

It would also be helpful to get some bar charts on the data. Brian knows what I am talking about and can probably help you.

Copy of our own permit cover sheet/checklist

Copies of the State waiver letters requesting mining permits.

Evelyn S. MacKnight
Chief, NPDES Permits Branch (3WP41)
Water Protection Division
Phone: 215-814-5717
Fax: 215-814-2301
email: macknight.evelyn@epa.gov

To   Matthew Klasen

cc   Christopher Hunter, Gregory Peck, Karyn Wendelowski, Stefania Shamet

bcc

Subject   Re: 114A-139A

Here are my edits. No big issues from me. Thanks.

ATTACHMENT REDACTED – DELIBERATIVE

2011-01-06 114A-139A for Kevin.ksm.docx

| Matthew Klasen | Hey Kevin, Here's another batch for you. Not to... | 01/06/2011 12:33:05 PM |

From:	Matthew Klasen/DC/USEPA/US
To:	Kevin Minoli/DC/USEPA/US@EPA
Cc:	Gregory Peck/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA
Date:	01/06/2011 12:33 PM
Subject:	114A-139A

Hey Kevin,

Here's another batch for you. Not too many questions here (only 25), but lots of text, and very technical macroinvertebrate answers.

(b) (5)

 .

Stef: I kept 140 for the next batch because it's the first one that directly references the ORD report, so I'm going to take a shot at the preface language on that one, consistent with the group's conversation this morning.

Thanks,
Matt

[attachment "2011-01-06 114A-139A for Kevin.docx" deleted by Kevin Minoli/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

Marcel,

You may have updated already, but I compared your list to mine and added anything I saw missing. I think you were working off one of the older versions of the list, which didn't include a lot of the references in the comment/response.

I had also had significantly revised some of the WVDEP references and added updated hyperlinks to access the reports.

 So, good luck, & hope this helps!

Carrie

[W]   ATTACHMENT REDACTED - DELIBERATIVE

 Appendix 7 FD Marcel Version 1-6-11 with CT edits.doc

Carrie Traver
USEPA Region 3
Office of Environmental Programs
1650 Arch Street - 3EA30
Philadelphia, PA 19103
215-814-2772
traver.carrie@epa.gov

Marcel Tchaou	Folks, This is latest version of the Reference list...	01/06/2011 03:28:25 PM

From:	Marcel Tchaou/DC/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Cc:	Carrie Traver/R3/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Greg Pond/R3/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/06/2011 03:28 PM
Subject:	Re: Fw: Spruce References list

Folks,
This is latest version of the Reference list as of 3:27 PM on 01/06/10

[attachment "Appendix 7 FD Marcel version 1-06-2011.doc" deleted by Carrie Traver/R3/USEPA/US]

****
Marcel K. Tchaou, Ph.D., P.E., P.H.
Environmental Engineer
Wetlands & Aquatic Resources Regulatory Branch
Office of Wetlands, Oceans and Watersheds
U.S. EPA
1200 Pennsylvania Avenue, NW (MC 4502T)
Washington, DC 20460
202-566-1904

From:	Matthew Klasen/DC/USEPA/US
To:	Marcel Tchaou/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Carrie Traver/R3/USEPA/US@EPA
Cc:	Greg Pond/R3/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/06/2011 11:16 AM
Subject:	Fw: Spruce References list

Chris, Marcel, and Carrie:

See Greg's note below. Can someone send Greg the most recent reference list?

This begs the question of what the most effective process should be for both verifying the reference list itself, and ensuring that all our responses (FD, PD comments, RD comments) don't cite new things and cite the right things (including things that are actually in the list).

I'm interested in hearing suggestions on what seems best to folks. We're getting close to the point where a significant portion of the RD responses are nearly done, following OGC review and resolution of OGC comments. I'd be willing to start sending out chunks of the compiled OGC-reviewed RD responses to folks to start checking references, which is something that needs to be done but that I'm probably not most qualified to do.

That said, for version control, Chris and I still need to maintain the compiler roles throughout this process.

Thoughts on process?

Thanks.
Matt

.

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229
----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/06/2011 11:08 AM -----

From:	Greg Pond/R3/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Date:	01/06/2011 11:07 AM
Subject:	Spruce References list

Matt, (b) (5) ███████████████████████████████████ Can you send me the "list"? When I go the ESC, there are all the references, but no list.

Thanks,

Greg

Greg Pond
Office of Monitoring and Assessment
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1060 Chapline Street, Suite 303

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Website: http://epa.gov/reg3esd1/3ea50.htm

Matthew Klasen/DC/USEPA/US

01/06/2011 06:06 PM

To   Kevin Minoli

cc   Christopher Hunter, Gregory Peck, Karyn Wendelowski, Stefania Shamet

bcc

Subject   140A-180A (with four exceptions

OK -- and here are 140A-180A. Four of them aren't ready for your final review (146A, 150A, 154A, and 165A). But we have good answers (I think) to each of these except 150A, so they're probably worth your time to read. These four comments/responses are highlighted in teal .

Note that this is the first "ORD-heavy" batch, beginning with 140A. I'm suggesting adding the boilerplate language in the text before 140A, and then each of the benchmark-focused responses that follows references parts of that language.

Thanks,
Matt

ATTACHMENT REDACTED - DELIBERATIVE

2011-01-06 140A-180A for Kevin.docx

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

| Kevin Minoli | Here are my edits. No big issues from me. Tha... | 01/06/2011 05:52:57 PM |

From:	Kevin Minoli/DC/USEPA/US
To:	Matthew Klasen/DC/USEPA/US@EPA
Cc:	Christopher Hunter/DC/USEPA/US@EPA, Gregory Peck/DC/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA
Date:	01/06/2011 05:52 PM
Subject:	Re: 114A-139A

Here are my edits. No big issues from me. Thanks.

[attachment "2011-01-06 114A-139A for Kevin.ksm.docx" deleted by Matthew Klasen/DC/USEPA/US]

| Matthew Klasen | Hey Kevin, Here's another batch for you. Not to... | 01/06/2011 12:33:05 PM |

From:	Matthew Klasen/DC/USEPA/US
To:	Kevin Minoli/DC/USEPA/US@EPA
Cc:	Gregory Peck/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Karyn Wendelowski/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA
Date:	01/06/2011 12:33 PM
Subject:	114A-139A

Hey Kevin,

Here's another batch for you. Not too many questions here (only 25), but lots of text, and very technical macroinvertebrate answers.

I've highlighted places where you should specifically weigh in on -- either where I think you could help add a PD reference or a couple WQS things (where we say things about the use but don't say it's been violated, so it's tough to figure out where we want to draw the line).

Stef: I kept 140 for the next batch because it's the first one that directly references the ORD report, so I'm going to take a shot at the preface language on that one, consistent with the group's conversation this morning.

Thanks,
Matt

[attachment "2011-01-06 114A-139A for Kevin.docx" deleted by Kevin Minoli/DC/USEPA/US]

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

David Kargbo/R3/USEPA/US

01/06/2011 06:24 PM

To   Jeffrey Lapp

cc   Christopher Hunter, Dave Campbell, David Rider, Frank Borsuk, John Forren, Kevin Minoli, Margaret Passmore, Matthew Klasen, Stefania Shamet, Stephen Field, John Pomponio

bcc

Subject   Comments on materials handling Plan for Spruce

Jeff;

Per your request, please see my comments on the materials handling Plan for Spruce. The referenced articles are attached.

Tomorrow id my compress day but I'll be checking my email if you need any additional help.

Dave.

Comments on MHP_Kargbo.doc

01 Bevans et al, Prediction & Treatment.tif

03 Spatial Trends.pdf

04 Selenium Concentrations in Middle PA Coal Beds.pdf

05 Se speciation in soils after alkaline extraction.pdf

06 USEPA 1992_Behavior of metals in soils.pdf

07 Vesper_Se Location and Mode of Occurrence.pdf

08 WV_selenium_plan.pdf

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Office of Environmental Innovation
Environmental Assessment and Innovation Division
USEPA Region 3
1650 Arch Street
Philadelphia, PA 19103
Tel: 215 814-3319 / E-mail: kargbo.david@epa.gov

Comments on the Materials Handling Plan for Spruce #1 mine

by

David Kargbo, PhD
USEPA Region 3

(b) (5)

Topic WQ-4

White Paper Topic: Prediction and Treatment of Selenium

Development Team: Hugh Bevans, Steve Parsons, Paul Ziemkiewicz, Bill Winters, et al.

Date: October 21, 2005

A FRAMEWORK FOR SELENIUM STUDIES IN THE APPALACHIAN PLATEAUS

Introduction

A recent Environmental Impact Study (EIS) on the effects of mountaintop coal mining in West Virginia showed that concentrations of selenium (Se) in small streams and sediment ponds receiving drainage from valley fills can exceed the aquatic wildlife standard of 5 micrograms per liter (μg/L). Deleterious impacts of this finding have not been observed in the Appalachian Plateaus, but can be implied from other research.

During the past 20 years, scientists from the U.S. Geological Survey (USGS) and the U.S. Fish and Wildlife Service (USFWS) have collaborated on studies to understand the occurrence and impacts of Se in the environment. Initial studies were conducted during 1982-85 at the Kesterson Reservoir, National Wildlife Management Area in the Central Valley of California, where Se leached by irrigation of desert soils caused severe health problems for aquatic wildlife. Studies at Kesterson Reservoir led to the development of the Department of Interior Irrigation Drainage Program in 1985 to investigate impacts of irrigation drainage throughout the western United States.

Se is an essential micronutrient for animals, but it is also known to be the most toxic to mammals of all biologically essential elements; fish and birds are very sensitive to Se contamination in an aquatic environment. Se is passed from parents to offspring in eggs and, during critical stages of development and growth, is substituted for sulfur in amino acids that form structural and functional proteins. As Se exposure increases, toxic effects can range from suppression of the immune system, to reduced juvenile growth, to embryo mortality, to mass wasting in adults, to teratogenesis (lethal or sub-lethal deformities) in juveniles, to juvenile mortality, and finally to adult mortality.

Previous studies have shown that predators are more at risk than their prey. Aquatic organisms strongly bioaccumulate Se, maybe up to thousands of times the water concentration, but are unaffected by residues in their tissues that can cause reproductive failure when consumed by predator fish and aquatic birds. Bioaccumulation in aquatic food chains is the most important rout for the transfer of toxic levels of Se to upper trophic level species, including humans. However, some forage plants accumulate Se from contaminated soils or wastes and are toxic when ingested by grazing animals.

Although there is a significant body of scientific literature on the occurrence and impacts of Se, most of the studies have been in the western United States where climatic conditions generally are drier and there is less biodiversity. This paper will present a framework for investigating Se in the Appalachian Plateaus region of the eastern United States.

SELENIUM RESULTS FROM THE EIS ON MOUNTAINTOP COAL MINING AND OTHER STUDIES

Selenium in Stream Water and Bottom Sediments

Se was analyzed in 213 stream-water samples as part of the EIS; 66 samples, all collected downstream from valley fills, exceeded the aquatic wildlife standard of 5 µg/L. The median concentration of Se detected at EIS sites downstream from valley fills was 11.7 µg/L while the median concentration for un-mined sites was below the detection limit of 3 µg/L. Subsequent sampling by the West Virginia Department of Environmental Protection (WVDEP) detected Se in 126 of 909 stream-water samples and resulted in nine streams being placed on West Virginia's 2002 303(d) list; four are in the Coal River Basin (Beech Creek, Left Fork Beech Creek, Rockhouse Creek, and Buffalo Fork) where 121 of the 126 Se detections occurred, four are in the Guyandotte River Basin, and one is in the Gualey River Basin. During July 2002 through June 2003 all 11 samples from Left Fork Beech Creek exceeded the 5 µg/L Se aquatic-wildlife standard; all four samples collected during February through June 2002 exceeded 35 µg/L (WVDEP). Se detections were most common during low flow; 95 of 126 detections were associated with total suspended solids concentrations (TSS) of 5 milligrams per liter (mg/L) or less; the highest seven Se concentrations were associated with TSS < 3 mg/L. In contrast, when TSS exceeded 50 mg/L (indicating overland runoff) there were only three associated detections of Se.

An ongoing study by West Virginia University (WVU) determined that most (90%) of the Se in water samples from the Mud River is selenate (SeO_4^{2-}) while a Se in water from a sediment pond at the toe of a valley fill was less oxidized, with about 70% selenate. Selenate is generally mobile and occurs in the dissolved state in water.

Se concentrations in ten bottom-sediment samples collected by the USFWS from the Coal River Basin ranged from < 0.229 to 1.49 parts per million (ppm), with a median concentration of 0.416 ppm. Se concentrations in four bottom-sediment samples from the Mud River Basin ranged from < 0.0679 to 0.192 ppm. Se concentrations in 52 fine-grained (< 63 micrometers) bottom-sediment samples collected during the USGS National Water-Quality Assessment (NAWQA) of the Kanawha-New River Basin ranged from 0.3 ppm to 2.4 ppm, with a medium concentration of 0.95 ppm. Correlation analyses showed that bottom-sediment Se concentrations were related to the percent of the basin occupied by quarries, coal strip mines, and gravel pits ($r^2 = 0.529$) and to mean annual coal production during 1980-95 ($r^2 = 0.271$).

Sources of Selenium

Se is often associated with organic-rich deposits including coal and black shale, both of which are present in the Pennsylvanian-age rocks that occur at or near the surface in the Appalachian Plateaus province. Available data on the geochemistry of Pennsylvanian-age coal beds show that those very beds that are included in the mountaintop mining sequence (Clarion, Brookville, No. 5 block, Stockton, Coalburg, and Winifrede) have high concentrations of Se; median concentrations in these coal beds range from about 4.5 to 7 ppm and concentrations exceeding 10 ppm have been observed. Of course, during mountaintop mining, this sequence of coals is removed and, therefore, cannot be the source of Se detected in streams draining valley fills during the EIS.

If a specific rock stratum in the mountaintop mining sequence is enriched in Se, then the release of Se to the environment probably could be controlled by materials handling protocols. However, preliminary geochemical analyses of core sections collected through a joint program by the U.S. Geological Survey (USGS), the West Virginia Geological and Economic Survey (WVGES), and WVU indicate that the entire mountaintop mining geologic interval is enriched with Se and that coarser-grained siltstone has the highest concentrations. If these preliminary results indicating enrichment of Se throughout the mountaintop mining sequence hold true, then controlling the release of Se by materials-handling protocols would be problematic. Se may be enriched in wastes from coal-washing operations and in coal ash from power generation.

Selenium in Aquatic Wildlife

Se concentrations in 16 whole-body composite fish samples (ten creek chub, five blacknose dace, and one bluegill) collected by USFWS from ten sites in the Coal River Basin ranged from 0.845 to 6.89 ppm, dry weight; the median concentration was 3.59 ppm. Se concentrations in seven whole-body composite fish samples (five creek chub and two blacknose dace) collected by USFWS from four sites in the Mud River Basin ranged from < 0.481 to 6.85 ppm, dry weight; the median concentration was 4.13 ppm. Se concentrations in 27 fish-liver samples (19 rock bass, six common carp, one smallmouth bass, and one white sucker) collected from 19 sites during the USGS Kanawha-New River NAWQA ranged from 1.7 to 15 ppm, dry weight; the median concentration was 5.8 ppm. Correlation analysis showed a relation between Se concentrations in livers of Rock bass and stream-bottom sediment ($r^2 = 0.568$).

QUESTIONS CONCERNING THE OCCURRENCE AND IMPACTS OF SELENIUM IN THE APPALACHIAN PLATEUS

There are many unanswered questions about the occurrence of Se and its impacts on Appalachian Plateaus ecosystems:

1. What are the relations among rock strata and Se enrichment?
2. Are there other trace elements of concern associated with this geologic interval?
3. What is the geographic extent of the Se-enriched geologic interval?
4. What are the background concentrations of Se in streams draining the enriched area?
5. Have land disturbances in the enriched area released Se to the aquatic environment?
6. What is the amount of Se available for leaching from fill materials?
7. What processes (physical, chemical, and microbiological) control the leaching of Se?
8. What is the rate of Se leaching and does this rate decline through time?
9. Are there quantifiable relations between land disturbances (location, extent, and age) and the occurrence of Se in the aquatic environment?
10. What are the concentrations and loads of Se in water from underground mines?
11. What are concentrations of Se in waters from coal-washing operations?
12. What are Se concentrations in leachate from coal ash from power plants?
13. Can we predict the occurrence and transport of Se in the aquatic environment?

Impacts of Selenium

1. What are the food-web pathways for Se in the Appalachian Plateaus?
2. Are there any quantifiable Se impacts to aquatic wildlife in the mountaintop coal-mining area where aquatic-wildlife standards for Se in water have been exceeded?
3. Are there likely to be impacts to aquatic wildlife as land disturbances continue?
4. Are there quantifiable impacts to grazing animals; is there potential for impacts?
5. Can we predict impacts of Se on aquatic or terrestrial wildlife?

Mitigating / Remediating Selenium Impacts

1. Can Se impacts be mitigated/remediated by materials handling methods?
2. Can Se impacts be mitigated by limiting the extent of disturbances (dilution)?
3. Can Se impacts be mitigated/remediated by water treatments?

FRAMEWORK FOR INVESTIGATING SELENIUM IN THE APPALACHIAN PLATEAUS

An assessment of the occurrence and impacts of Se should:

1. Include the elements of occurrence, impacts, and mitigation discussed above.
2. Encompass the region where surface and near-surface rocks are Se enriched, probably based on coal trace-element and NURE data;
3. Include other trace elements that may be of concern in the region, as identified through a review of available data; and
4. Develop a model for predicting the occurrence and impacts of Se, like the following example for the San Francisco Bay area. A conceptual model for Se in the Appalachian Plateaus Data would be a good framework for designing scientific studies to provide necessary information.
5. Design, implement, and evaluate potential means of remediating Se contamination.

Bay-Delta Selenium Model
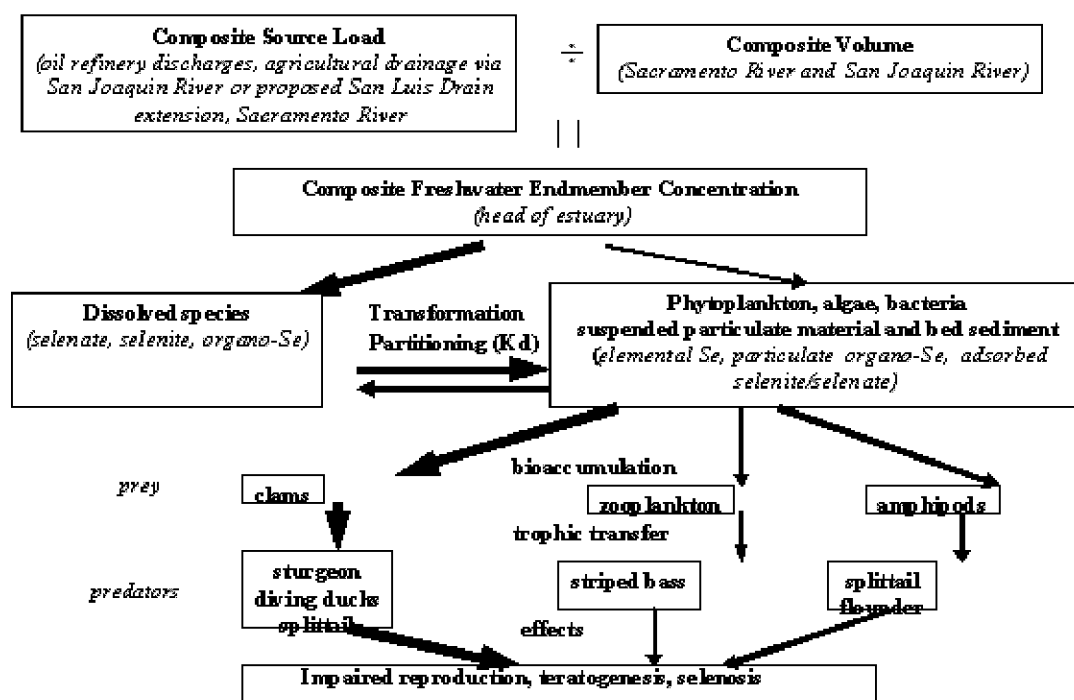
APPROACH

Phase 1 (first year)-- Develop a conceptual "Rock to Duck" Se model; assemble and evaluate available data and literature on Se in coal, rock strata, stream-bottom sediments, and tissues of aquatic and other wildlife; use available data to develop a preliminary model for predicting Se impacts, to estimate the geographic extent of Se enriched geologic sequence, and to evaluate relations among factors controlling the occurrence and impacts of Se; conduct biological impacts reconnaissance; integrate ongoing investigations; plan for Se monitoring and investigations.

Phase 2 (second through fifth years)-- Conduct data-collection activities and studies to provide information necessary to fill in gaps in describing, predicting, and mitigating the occurrence and impacts of Se; complete "Rock to Duck" Se model; report on findings.

Phase 3 (sixth through tenth year)-- Remediate; evaluate remediation; report on findings.

SUPPORT AND FUNDING

Support Pathways

1. Participating Agencies
2. DOI
3. Eastern Mine Drainage Federal Consortium
4. Mid-Atlantic Federal Partners on the Environment
5. Coal Industry

Funding Pathways

1. DOI Initiative
2. Federal Agencies- EPA, OSM, USGS, USFWS, COE, DOT, DOE (NETL)
3. State Agencies
4. Coal Industry
5. Any combination of above sources

Selenium Bibliography

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U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

**Spatial Trends in Ash Yield, Sulfur, Selenium,
and Other Selected Trace Element Concentrations
in Coal Beds of the Appalachian Plateau Region, U.S.A.**

by

Sandra G. Neuzil[1], Frank T. Dulong[1], and C. Blaine Cecil[1]

Open-File Report 2005-1330

[1]U.S. Geological Survey, Reston, Virginia 20192

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Abstract
Introduction
Methods
       Samples
       Coal Bed Correlations
       Statistical Analyses and Terminology
Results and Discussion
       Regional Distribution of Selenium
       Selenium Concentrations in Coal Beds
       Selenium Distribution Within Coal Beds
       Selenium in Thick and Thin Coal
       Stratigraphic Trends in Selenium
Conclusions
Future Work
References Cited

LIST OF FIGURES

LIST OF TABLES

thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30, * if N < 30; N = number of samples.]

5. Coal quality statistics for coal samples in three stratigraphic intervals (pre-SGB, SGB, and post-SGB) for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thick (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [N = number of samples. Coal beds in stratigraphic intervals pre-SGB, SGB, and post-SGB are listed in table 2.]

Spatial Trends in Ash Yield, Sulfur, Selenium, and Other Selected Trace Element Concentrations in Coal Beds of the Appalachian Plateau Region, U.S.A.

by

Sandra G. Neuzil, Frank T. Dulong, and C. Blaine Cecil

U.S. Geological Survey, Reston, Virginia 20192

ABSTRACT

Land disturbances sometimes contribute to relative increases in deleterious substances in streams. Acid drainage in response to coal mining in certain regions of the Appalachian Plateau is one well known example. Apparent relative increases in selenium (Se) in some streams where land disturbance has occurred in the coal-producing region of the Appalachian Plateau may also be of concern. As a result of concerns regarding selenium, this report evaluates the spatial variation (both stratigraphic and regional) of selenium in coal beds in the Appalachian coal fields of Pennsylvania, Maryland, Ohio, West Virginia, Kentucky, Tennessee, and Virginia.

Analyses of selenium, ash yield, and sulfur concentrations in more than 3,000 coal samples were used to evaluate both the stratigraphic and regional variation of these parameters. The samples are from more than 70 coal beds in the Lower, Middle, and Upper Pennsylvanian Series, located in the Appalachian Plateau region of western Pennsylvania, western Maryland, eastern Ohio, throughout West Virginia, eastern Kentucky, northeastern Tennessee, and southwestern Virginia. Coal beds in the middle Middle Pennsylvanian series, from the Cedar Grove coal bed in West Virginia and the correlative Whitesburg coal bed in eastern Kentucky up through the Clarion coal bed in Pennsylvania and Ohio generally have an average selenium concentration greater than 3.9 ppm (remnant-moisture, whole-coal), an empirical observation. All coal samples from this stratigraphic interval have an average selenium concentration of 5.4 ppm. For the purposes of this report, this stratigraphic interval is referred to as "selenium greater than background" abbreviated SGB, in reference to average selenium concentrations in coal that are greater than the average for all northern and central Appalachian basin coal samples of 3.6 ppm Se.

Coal beds in the SGB stratigraphic interval generally have a median selenium concentration greater than 3.5 ppm. In contrast, coal beds that are from older strata that underlie the SGB interval (pre-SGB in this report) or from younger strata that overlie the SGB interval (post-SGB in this report) generally have median selenium concentrations that are less than 3.5 ppm. The median selenium concentrations for all coal samples from the pre-SGB, SGB, and post-SGB intervals are 2.7, 5.0, and 2.6 ppm selenium, respectively. This trend of lower-higher-lower selenium concentrations in the three stratigraphic intervals is different from the median ash yield that is 6.7, 11, and 11 percent ash on an as-received, whole-coal basis, respectively, or a

stratigraphic trend of lower-higher-higher. The stratigraphic trend in median sulfur concentration for all coal samples is lower-lower-higher with values of 0.9, 1.1, and 2.7 percent sulfur on an as-received, whole-coal basis, respectively, and is different from the trends in both selenium and ash yield. In the Appalachian Plateau region, the selenium concentrations in coal samples from the Cedar Grove/Whitesburg to Clarion (SGB) interval are almost twice those in coal samples from the older (pre-SGB) and younger (post-SGB) coal beds for thick ($\geq$ 28 inch) as well as thin (< 28 inch) coal samples.

The different stratigraphic trends in selenium, ash yield, and sulfur concentration suggest that different processes control their concentrations in coal and that neither ash yield nor sulfur concentration can be used as a predictor for selenium concentration in coal. Whether the stratigraphic trend in selenium concentrations in eastern U.S. Pennsylvanian coal reflects a similar trend in selenium concentrations in overall Pennsylvanian strata remains unanswered.

INTRODUCTION

The practice of mountaintop coal mining (MTM) disturbs large volumes of rock. Elevated selenium concentrations reported from streams that drain areas impacted by MTM in southern West Virginia (Bryant and others, 2002; Ferreri and others, 2004; Vesper and others, 2004) and areas impacted by coal surface mining and reclamation in Ohio (Bonta and Dick, 2003) have drawn attention to the potential for increases in selenium concentrations in drainage from these Appalachian Plateau coal mining regions. The source of selenium in drainage water may be coal, although in surface mining all of the coal is removed, and the source of selenium is more likely to be the associated strata disturbed by mining operations. In underground room and pillar mining, an average of 50 percent (range 35 - 70 percent) of the coal is left in place (Wood and others, 1983). In underground longwall mining, approximately 30 percent of the coal remains. Selenium in coal left in underground mines could conceivably contribute to selenium in groundwater and streams in areas of both active and abandoned underground mines. Understanding levels and trends in selenium concentrations in coal beds and associated rocks would aid in predicting the potential for selenium mobilization as a result of coal mining and other major rock disturbance. Although study of the selenium concentrations in rocks is beyond the scope of this report, an assessment of the concentration range of selenium content in coal beds throughout the Appalachian basin is a first step toward determining whether there are any potential risks of selenium contamination from past, present, or future coal mining and utilization in the Appalachian basin.

Selenium concentration in coal varies among coal basins. The average and geometric mean concentrations of selenium in United States (U.S.) coal are reported as 2.8 and 1.8 ppm (whole-coal basis) respectively (Finkelman, 1993). Average selenium concentration in coal in the Appalachian basin, Interior province, and Powder River basin in the U.S. are reported as 3.5, 3.2, and 1.1 ppm (whole-coal basis), respectively (Finkelman and others, 1994). Gluskoter and

others (1977) calculated the enrichment factor for selenium in U.S. coal (the ratio of geometric mean selenium in coal / average selenium in crust) and showed that it is greater than the enrichment factor of all other elements. In eastern, interior, and western coal basins, selenium enrichment (whole-coal) is 68, 40, and 26, respectively (Gluskoter and others, 1977). Coal mining and utilization are major pathways that mobilize selenium into the environment (Lemly, 2004). For coal utilization purposes, selenium concentrations on a Btu basis are more meaningful than on a whole-coal basis. Se/Btu are more similar than Se/coal among the Appalachian, Interior, and Powder River basins due to a decrease in Btu values in conjunction with the decrease in selenium from the Appalachian to Interior to Powder River basin (Bragg and others, 1998). Elevated concentrations of selenium mobilized by coal mining disturbance in the Powder River basin have been observed by Dreher and Finkelman (1992).

The assumption that selenium in coal is primarily associated with pyrite (Coleman and others, 1993; Taylor and others, 1998; Diehl and others, 2004) is often made because selenium shows some chemical behavior similar to sulfur (McNeal and Balistrieri, 1989) and coal beds are reducing environments where sulfur and selenium would generally be in a reduced state and therefore less mobile. Various studies of selenium in coal and rocks associated with coal have shown that selenium substitutes for sulfur in pyrite, is associated with mineral matter, or is associated with organic matter (Kuhn and others, 1980; Cecil and others, 1981; Cahill and others, 1982; Oman and others, 1988; Naftz and Rice, 1989; Diessel, 1992; Dreher and Finkelman, 1992; Coleman and others, 1993; Taylor, 1998; Zhang and others, 2002; Hower and Robertson, 2003; Lussier and others, 2003; Diehl and others, 2004; Jenkins and Schaer, 2004). The fact that selenium may have more than one mode of occurrence in coal and coal-bearing strata and that selenium occurs in trace amounts may explain why it is difficult to demonstrate a correlation between selenium and other parameters.

The data used in this report are a subset of the U.S. Geological Survey COALQUAL database (Bragg and others, 1998; http://energy.er.usgs.gov/products/databases/CoalQual/intro.htm). Statistical data are presented herein for selenium, coal bed thickness, ash yield, sulfur (S), pyritic sulfur (Spyr), arsenic (As), mercury (Hg), and manganese (Mn). Arsenic and mercury data are included because they are trace elements in coal that are released to the environment via coal combustion and may have deleterious health effects (U.S. Environmental Protection Agency, websites: http://www.epa.gov/ttn/atw/hlthef/arsenic.html., http://www.epa.gov/safewater/arsenic.html., http://www.epa.gov/mercury/ , http://www.epa.gov/mercury/control_emissions/index.htm., http://www.epa.gov/OGWDW/dwh/t-ioc/mercury.html.). Manganese data are included in this report because manganese is released to the environment via coal mining and major rock disturbance. Manganese causes staining, an aesthetic problem, and is currently under study to determine whether there are health issues related to manganese exposure that warrant revision of manganese standards for drinking water (California Department of Health Services, 2005). In addition to selenium, only the thickness, ash yield, and sulfur data are discussed in detail in this

report.

This Open File Report focuses on selenium concentration in Pennsylvanian coal beds in the northern and central Appalachian basin coal region (fig. 1). Extensive data for selenium concentrations in coal beds, including those from the stratigraphic interval of MTM in the central Appalachian basin and the equivalent time interval in the northern Appalachian basin, are available at a regional scale (Appendix 1). Selenium, ash yield and sulfur data are examined for the average and median concentrations in each state, the distribution of concentrations in coal samples from three individual coal beds, stratigraphic trends in concentrations among coal beds, and comparison of concentrations in coal that is thicker or thinner than 28 inches. Stratigraphic trends in selenium concentration of coal beds are compared to stratigraphic trends in ash yield and sulfur concentration and are found to be dissimilar.

METHODS
Samples
Concentrations of selenium and other parameters in coal beds were obtained from the U.S. Geological Survey COALQUAL Database (Bragg and others, 1998; http://energy.er.usgs.gov/products/databases/CoalQual/intro.htm). Data from 3227 coal samples (Appendix 1) from 124 counties in western Pennsylvania, western Maryland, eastern Ohio, throughout West Virginia, eastern Kentucky, northeastern Tennessee, and southwestern Virginia in the northern and central Appalachian basin (Tully, 1996) are included in this report. Each coal sample represents the complete-bed thickness and was collected from working mines (2400 channel samples), drill cores (529 samples), or outcrops (298 weathered channel samples) in the 1970's and 1980's. The analytical methods used to determine selenium concentration were X-ray fluorescence spectroscopy (XRF) (184 samples) and instrumental neutron activation analysis (INAA) (3043 samples). Selenium concentration is reported to two significant figures on a remnant-moisture, whole-coal basis. Approximately 6 percent of the selenium values are qualified; that is, the value is greater than or less than the value reported (Bragg and others, 1998; http://energy.er.usgs.gov/products/databases/CoalQual/Docs/techinfo.pdf). In COALQUAL, selenium concentrations below the lower detection limit of the analytical method are reported as 0.7 times the detection limit. Selenium concentrations were not reported by Bragg and others (1998) for two samples, one channel and one drill core, analyzed by INAA. Additionally, selenium values for two channel samples analyzed by XRF were discarded in this report because of their exceptionally high selenium concentrations (150 ppm in the Lower Freeport coal bed in Ohio and 52 ppm in the Princess No. 9 coal bed in West Virginia), which are greater than two times the next highest value. The range of selenium concentrations of the remaining 3223 samples (fig. 1) is 0.07 to 21 ppm (Appendix 1). Ash yield and sulfur were determined by ASTM methods D3174 and D4239, respectively, and are reported to two decimal places on an as-received, whole-coal basis (ASTM, 1992). One manganese concentration, analyzed by INAA in a channel sample from the Little Raleigh coal bed in West Virginia, was discarded for this report

because of its exceptionally high value (1400 ppm) that was more than two times the next highest value (690 ppm).

Coal Bed Correlations

Coal bed samples from the COALQUAL database were correlated on an interstate basis in the northern and central Appalachian coal regions for this report (table 1). The chronostratigraphic position of each coal bed name, as used in this report, and the number of samples is given in table 2. The number of coal samples in each coal bed are listed by state (table 1) and by thickness (greater than or less than 28 inches) (table 2). Although the correlation of coal beds across county and state boundaries has uncertainty, the relative stratigraphic positions and correlations of this report are generally correct or never offset by more than one coal bed.

Correlation of coal beds from the lower Middle Pennsylvanian Pond Creek coal in eastern Kentucky and correlative coal beds in the central Appalachian basin up through the upper Middle Pennsylvanian No. 6 Block coal bed in the central Appalachian basin in southern West Virginia and the correlative Lower Kittanning coal bed in Pennsylvania in the northern Appalachian basin are summarized in Figure 2 (from Neuzil, 2001, fig. 1 and references therein).

The stratigraphic positions of the Quakertown coal bed and the Mercer coal beds in the Pottsville Formation of the northern Appalachian basin in relation to coal beds in the central Appalachian basin are uncertain because the coal beds are discontinuous and stratigraphic palynology does not resolve these coal bed correlations. Peppers (1996) places the Quakertown coal bed in Ohio in the upper Westphalian A series (western European terminology), the upper Morrowan series (midcontinent terminology), and in the lower Kanawha Formation (southern West Virginia terminology). However, the Pottsville Formation in the northern Appalachian basin does not include much of the strata in the Lower and lower Middle Pennsylvanian (Eble, 1994) and we have, therefore, placed the Quakertown coal bed in the Middle Pennsylvanian, Westphalian C, or Atokan (table 2), which is higher than Peppers' (1996) placement.

Peppers (1996) correlates the Upper Mercer coal bed in Ohio with the Upper No. 5 Block coal bed in southern West Virginia and the Lower Mercer coal bed in Ohio with the Stockton coal bed in southern West Virginia. Although the Upper and Lower Mercer coal beds may correlate with the No. 5 Block and Stockton coal beds, in this report we will consider these northern and central Appalachian basin coal beds separately because the stratigraphic correlations are uncertain (tables 1 and 2).

Correlation of the Brookville and Clarion coal beds in the upper Middle Pennsylvanian Allegheny Formation in the northern Appalachian basin to coal beds in the central Appalachian basin is uncertain (Neuzil, 2001). The Brookville and Clarion coal beds may correlate with the No. 5 Block coal zone (Rice, and others, 1994) or they may be above the No. 5 Block coal zone (Blake, 1992; Eble, 1994). In this report the northern Appalachian basin Brookville and Clarion

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coal beds are placed stratigraphically above the No. 5 Block coal bed in the central Appalachian basin and are considered separately (tables 1 and 2).

Coal bed samples collected in the central Appalachian basin in counties in southern West Virginia and eastern Kentucky that were designated by northern Appalachian basin coal bed names (Appendix 1), such as Upper Kittanning and Lower Kittanning, have been correlated to central Appalachian basin coal bed names through discussions with Bascombe M. Blake Jr. (WVGES), Donald R. Chesnut Jr. (KGS retired), and Cortland F. Eble (KGS) (Neuzil, 2001, Appendix 2).

Statistical Analyses and Terminology

Statistical analyses were conducted as follows. First, the average, standard deviation, minimum, lower quartile, median, upper quartile, and maximum were calculated for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese for all coal bed samples within each state, treating the northern and southern West Virginia coal fields separately (table 3). Second, the distribution of selenium (fig. 3a), ash yield (fig. 3b), and sulfur (fig. 3c) concentration values were calculated for each of three coal beds (Pond Creek, Coalburg, and Pittsburgh) that have a large sample population, more than 100 samples. The Pond Creek, Coalburg, and Pittsburgh coal beds span the lower Middle to Upper Pennsylvanian stratigraphic interval (fig. 2 and table 2) and have been studied in detail (Neuzil, 2001; Ruppert and others, 2001; Tewalt and others, 2001). Third, the geometric mean, average, standard deviation, minimum, lower quartile, median, upper quartile, and maximum were calculated for selenium and other parameters for each coal bed with 5 or more samples in the Appalachian Plateau region (table 4a). Finally, the same statistical parameters were also calculated for coal bed samples greater than and less than 28 inches thick, if there were 5 or more samples in a coal bed in the thickness category (tables 4b and 4c).

The terms median, midspread, and lower and upper quartiles as used herein are clarified as follows. Consider the values of a given parameter (for example, the selenium concentration) of a sample population (for example, each sample in a coal bed) and sort these values into ascending order. The median is the value of the middle sample, which is at the 50th percentile of the sample population. The midspread is the range of values from the lower to the upper quartile, which is the range from the 25th to 75th percentile of the ascending order sample population. The values for half of the samples fall within the midspread. One quarter of the samples have a value less than the lower quartile, and one quarter of the samples have a value greater than the upper quartile. When a sample population has a normal distribution, the median and geometric mean will be equal to the average. If a sample population has a normal distribution, 30 random samples from that sample population are generally considered a large enough sample set to statistically represent the entire sample population (Drennan, 1996). A larger sample set, for example >100 samples, may appear more convincing. However, statistical values (average, median, geometric mean, lower quartile, and upper quartile) calculated from a larger sample population will not be

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significantly different from those calculated from 30 random samples (Drennan, 1996).

RESULTS and DISCUSSION
Regional Distribution of Selenium

      The latitude and longitude locations of 3223 coal samples with selenium data are shown in Figure 1. The sample locations reflect the general extent of coal resources in the northern and central Appalachian basin (Tully, 1996). The density of sample locations is not uniform throughout the basin because deep coal in the middle of the basin is under represented. The subset of 809 samples with elevated selenium concentrations that are greater than the upper quartile for the entire Appalachian basin (> 4.5 ppm Se) are shown in red in Figure 1. Samples with elevated selenium have a geographic distribution that is similar to the distribution of all coal samples (fig.1). To examine geographic variability, one can consider the selenium concentration in all coal samples within each state. All of the coal samples in Pennsylvania, Maryland, and Ohio are located within the northern Appalachian basin and all of the coal samples in Kentucky, Tennessee, and Virginia are within the central Appalachian basin. Therefore, we will consider the northern and southern West Virginia coal fields separately. The average and median selenium concentration in coal in each state ranges from a low of 2.5 and 1.7 ppm, respectively, in northern West Virginia, to a high of 4.2 and 3.8 ppm, respectively, in eastern Kentucky (table 3). The increase from low to high selenium values by state, for either average or median selenium concentration, is approximately a factor of two, and reflects the stratigraphic variability of selenium.

Selenium Concentrations in Coal Beds

      The selenium concentration in coal beds with more than 30 samples ranges from a low average and median in the Pittsburgh coal bed of 1.7 and 1.4 ppm Se, respectively, to a high average and median in the No. 5 Block coal bed of 7.1 and 6.4 ppm Se, respectively (table 4a). The increase from low to high selenium values by coal bed, for either average or median selenium concentration, is approximately a factor of four.

Selenium Distribution Within Coal Beds

      When a sample population has a normal distribution, the average will be close to the median value. If a sample population has a log normal distribution, the geometric mean will be close to the value of the median. Histograms illustrating the distribution of selenium concentrations in 3 coal beds, which each have a large sample population of more than 100 samples, appear to be close to normal with a tail of high values (fig. 3a). The average, median, and geometric mean selenium values are plotted for coal beds that each have more than 30 samples (fig. 4a), a sufficiently large random sample set if the sample population has a normal distribution. For most coal beds in the Appalachian basin the average, median, and geometric mean values for selenium concentration are quite close. This is consistent with each coal bed having a nearly normal distribution of selenium concentrations and indicates that these three

statistical parameters (average, median, and geometric mean) are all useful for understanding stratigraphic trends in selenium concentration in the Appalachian Plateau region coal beds. For coal beds with more than 30 samples, the average selenium concentration is greater than the median, except in the Waynesburg coal bed, and the average is slightly greater than the geometric mean in all cases. This confirms that each coal bed has no more than a few high values of selenium (Appendix 1). For example, only 6 of the 31 coal beds with more than 30 samples have a maximum selenium value that is more than 10 ppm greater than the upper quartile selenium value (table 4a). The median and midspread of selenium concentration in each coal bed with 30 or more samples are illustrated in Figure 5a. There is a considerable range in selenium concentrations in each coal bed throughout the Pennsylvanian (figs. 3a and 5a and tables 4a, 4b, and 4c).

Selenium in Thick and Thin Coal

The top and bottom layers of a coal bed often have higher ash yield or pyrite content compared to the rest of the coal bed (Gluskoter and others, 1977; Cecil and others, 1981; Taylor and others, 1998). If an element is enriched in the top and bottom layers of a coal bed, then thin areas of coal beds would have a greater overall concentration of the element than thick areas as a result of the greater proportion of "surface" coal and less dilution by the lower concentration in the middle of the coal bed. In order to determine whether the thickness of a coal bed has any influence on selenium distribution within a coal bed, the geometric mean of selenium is plotted for coal that is greater than or less than 28 inches thick, for each coal bed where there are more than 30 samples in the thickness category (fig. 6a). The geometric mean for selenium in thick coal is greater than in thin coal for 12 of the 14 coal beds that have more than 30 samples in each of the two thickness categories (tables 4b and 4c). This suggests that selenium is not concentrated in the top and bottom surfaces of each coal bed, but rather uniformly distributed. For comparison, higher concentrations of ash yield are found in thick coal compared to thin coal in 8 of 14 cases (fig. 6b; tables 4b and 4c). In contrast to selenium and ash yield, sulfur concentrations are higher in thin coal compared to thick coal in 12 of 14 cases (fig. 6c; tables 4b and 4c).

Stratigraphic Trends in Selenium

When the selenium concentrations in coal beds are considered in a stratigraphic context, selenium concentrations appear to be generally higher in coal beds in the upper Kanawha and lowermost Allegheny Formations and equivalent strata compared to coal beds in underlying and overlying stratigraphic intervals (figs. 4a, 5a, and 6a; table 2). Eight coal beds, each with more than 30 samples, from the Cedar Grove/Whitesburg up through the Clarion have an average, median, and geometric mean selenium concentration greater than 3.9, 3.5 and 3.6 ppm respectively and a lower quartile greater than 2.7 ppm (table 4a). This stratigraphic interval will be referred to in this report as "selenium greater than background" or SGB in reference to the elevated levels of selenium in the coal beds. Thirteen coal beds from the underlying interval and ten coal beds from the overlying interval, each with more than 30 samples, have lower average, median, and geometric mean selenium concentrations that are less than 3.9, 3.5, and 3.6,

respectively, with 3, 2, and 1 exceptions, respectively. These two stratigraphic intervals will be referred to as pre-SGB and post-SGB. This stratigraphic trend of lower-higher-lower selenium concentrations in coal beds in the (1) pre-SGB interval (Pocahontas No. 3 to Williamson/Amburgy), (2) SGB interval (Cedar Grove/Whitesburg to Clarion), and (3) post-SGB interval (Lower Kittanning to Waynesburg) is also apparent in thick (≥ 28 inch) and thin (< 28 inch) coal bed samples (fig. 6a; tables 4b and 4c). In thick coal beds, with more than 30 thick samples in a coal bed, the range for geometric mean values for selenium in the pre-SGB, SGB, and post-SGB intervals is 2.0 to 3.8 ppm, 3.5 to 7.0 ppm, and 1.4 to 4.5 ppm, respectively. In thin coal beds, with more than 30 thin samples in a coal bed, the geometric mean values for selenium have a range of 1.9 to 2.9 ppm, 3.8 to 4.6 ppm, and 2.6 to 3.4 ppm in the pre-SGB, SGB, and post-SGB intervals, respectively.

On the basis of data from the COALQUAL database (Bragg and others, 1998), selenium concentrations in coal beds in the Appalachian basin coal region have a distinctive stratigraphic trend. Selenium is relatively low in coal beds contained in Lower and lower Middle Pennsylvanian strata, the pre-SGB interval (fig. 2; table 2). These strata include the Lower Pennsylvanian, Pocahontas and New River Formations, and the lower Middle Pennsylvanian, lower division and lower part of the middle division of the Kanawha Formation in West Virginia and equivalent strata in other states in the northern and central Appalachian basin. There is a relative increase in selenium in the middle of the Middle Pennsylvanian, upper part of the middle division and the upper division of the Kanawha Formation and lowermost Allegheny Formation in West Virginia (and equivalent strata), the SGB interval. The upper Kanawha Formation and lower Allegheny Formation (and equivalent strata) coal beds in the northern and central Appalachian basin that have elevated levels of selenium, comprise the coal beds that are the predominant targets of MTM (table 2). After reaching a maximum selenium concentration in the lower Allegheny Formation No. 5 Block coal bed, selenium concentrations are relatively low in the coal beds in the overlying upper Middle Pennsylvanian Allegheny Formation and the Upper Pennsylvanian Conemaugh and Monongahela Formations, the post-SGB interval.

Statistical calculations were conducted for the pre-SGB, SGB, and post-SGB stratigraphic intervals that included all coal samples, regardless of the number of coal samples in each coal bed (table 5). The average and median selenium concentrations both show a trend of lower-higher-lower values from oldest to youngest for the three stratigraphic intervals whether all coal (table 5a), thick coal (table 5b), or thin coal (table 5c) samples are considered. This trend is apparent even though elevated concentrations of selenium (> 4.5 ppm) are present in coal samples in each of the three stratigraphic intervals (figs. 1 and 5a; tables 4a, 4b, and 4c). The trend in selenium contrasts to an average, median, geometric mean, and midspread ash yield trend that is lower-higher-higher (figs. 4b, 5b, and 6b) in the pre-SGB, SGB, and post-SGB intervals, respectively (tables 5a, 5b, and 5c). The average, median, geometric mean, and midspread sulfur concentration trend is lower-lower-higher (figs. 4c, 5c, and 6c) for the pre-SGB, SGB, and post-SGB intervals, respectively (tables 5a, 5b, and 5c), which is different from both the selenium concentration and

ash yield trends. The difference in the stratigraphic trends for selenium, ash yield, and sulfur are illustrated by histograms of their concentration distribution in each of the three stratigraphic intervals for all ([fig. 7a](#)), thick ([fig. 7b](#)), and thin ([fig. 7c](#)) coal samples.

CONCLUSIONS

1. Mountaintop mining practices remove most of the coal. Therefore, coal is unlikely to be the source of slightly elevated concentrations of selenium found in streams impacted by MTM. Underground coal mining practices leave a significant portion of the coal, which may be a source of selenium in abandoned and active underground coal mine drainage.

2. The spatial (regional and stratigraphic) distribution of elevated selenium concentration coal samples (defined as > 4.5 ppm Se in this report) includes both the northern and central Appalachian basin and is not restricted to the MTM region or the MTM stratigraphic interval of southern West Virginia and eastern Kentucky.

3. There is more variability in selenium concentration stratigraphically among coal beds than geographically among states.

4. Selenium concentrations within a coal bed have a normal distribution.

5. Selenium does not appear to be concentrated in the surfaces of coal beds and has slightly higher concentrations in thick ($\geq$ 28 inch) than thin (< 28 inch) portions of coal beds.

6. Statistical results suggest that selenium concentrations are approximately two times higher in coal beds in the "selenium greater than background" interval of the middle Middle Pennsylvanian (equivalent to the uppermost Westphalian B, Westphalian C, and lowermost Westphalian D in western Europe terminology or the upper Atokan and lowest Desmoinesian in mid-continent time series terminology) than in older or younger coal beds in the Appalachian basin.

7. The stratigraphic trend in selenium concentration is the same for all thicknesses, thick ($\geq$ 28 inch), or thin (< 28 inch) coal bed samples.

8. The stratigraphic trend in selenium concentrations does not correspond to the stratigraphic trends in either ash yield or sulfur concentration.

9. Understanding stratigraphic trends of selenium in coal is important to coal users to predict potential total selenium in fly ash and other byproducts that may be reintroduced to the environment at disposal sites.

10. Whether stratigraphic trends in selenium concentration in coal beds indicate trends in selenium concentration in associated strata needs to be confirmed with rock analyses.

FUTURE WORK

There is a critical need to evaluate selenium concentrations in the non-coal strata of the Appalachian Plateau region, especially where the rocks are subjected to significant surface and underground disturbance and could be a source of selenium, for example in land disturbance such as MTM. Extensive data are not currently available for the selenium concentrations in the overburden and interburden rocks of the SGB interval in the Appalachian Plateau region.

Preliminary data from three cores indicate that the concentration of selenium in rocks in the SGB stratigraphic interval, the interval most commonly subjected to current intensive MTM, may be higher than in rocks above and below this interval (work in progress by Cecil, Dulong, and Renton). Further sampling and analyses of the rocks in the SGB interval is needed to assess potential rates of weathering and leaching and the produced ionic species in leachates to better understand the potential sources of selenium to the environment from coal mining practices and other major rock disturbance throughout the Appalachian Plateau region.

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Figure 1. Coal bed sample locations (N = 3223).

EXPLANATION

Selenium

- 0.07 - 4.5 ppm
- > 4.50 ppm
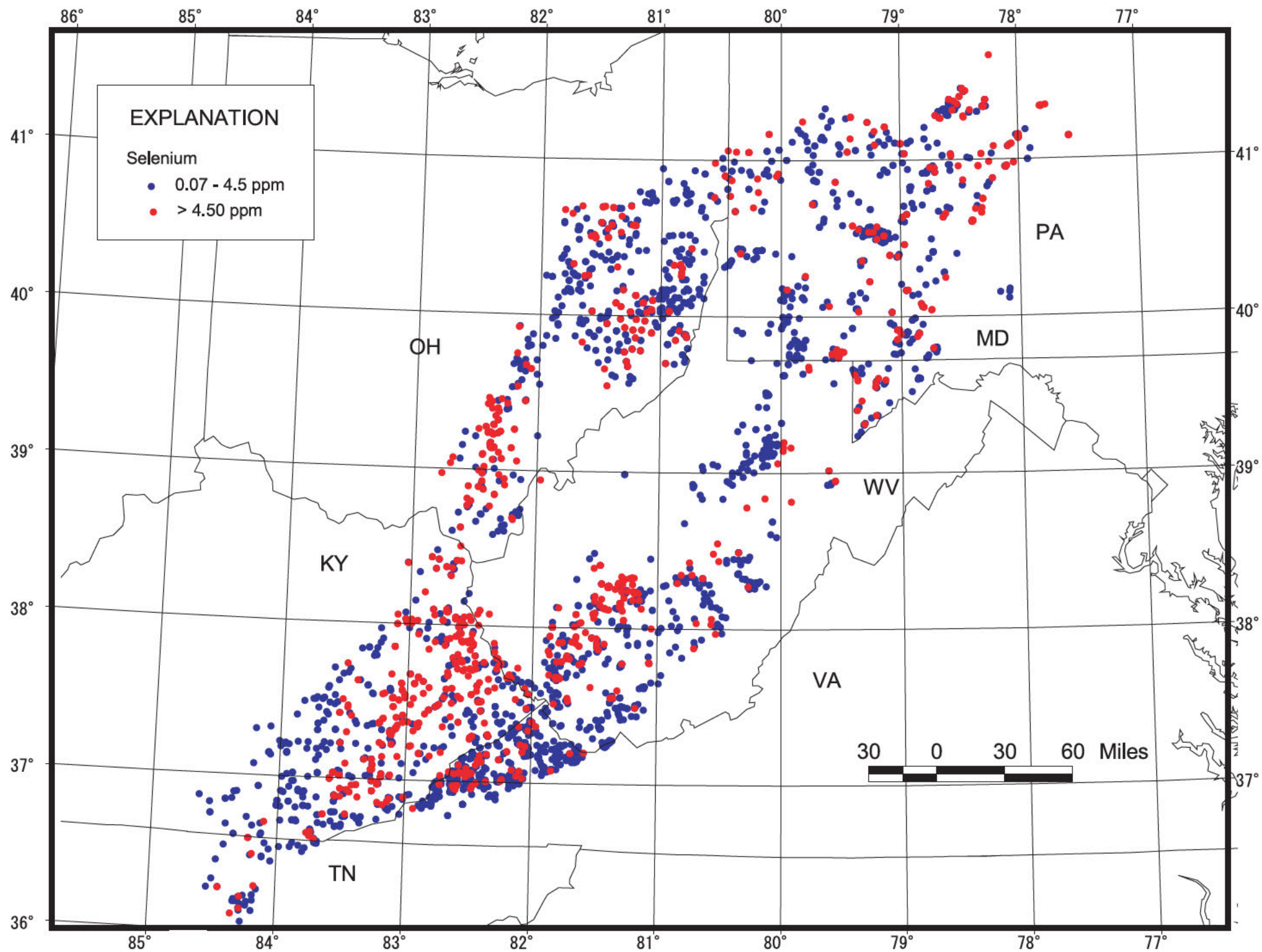
Figure 2. Stratigraphic correlation of coal beds and coal zones in part of the Middle Pennsylvanian Series in the northern and central Appalachian basin coal region, from the northeast to the southwest (modified from Neuzil, 2001, fig.1 http://pubs.usgs.gov/prof/p1625c/CHAPTER_I/CHAPTER_I.pdf.) Chart showing correlation of coal zones in part of the Middle Pennsylvanian Series in the northern and central Appalachian Basin coal regions, from the northeast to the southwest. Stratigraphic relationships and coal-zone correlations are indicated for southern West Virginia, eastern Kentucky, southwestern Virginia, and northern Tennessee. Beyond this explanation, the correlation chart is broken into four pages: *Page 3* = Upper left quadrant of chart; *Page 4* = Upper right quadrant of chart; *Page 5* = Lower left quadrant of chart; *Page 6* = Lower right quadrant of chart. Formal and informal unit names, stratigraphic relationships, and coal zone correlations are drawn from Rice and others (1994); also see references therein, except as noted: a, Kosanke (1988); b, Eble (1994); c, Blake (1992); d, Blake (1998); e, Donald R. Chesnut, Jr. and Cortland F. Eble (KGS, written commun., 1999); f, Blake and others (1994); g, Chesnut (1992); h. Chesnut (1997); i, Nolde (1994a); j, Nolde (1994b); k. Charles L. Rice (USGS retired, oral commun., 1999); and l, Rice (1984). This correlation chart is generalized and not all units are shown. 'Coal' indicates coal bed. Coal zones are noted. Query '?' indicates uncertain correlation of this unit. Empty formal or informal unit boxes indicate no significant unit present at this horizon. Unshaded units are coal. Shaded units are clastic and carbonate sedimentary units; many are marine in origin. Where two coal bed names appear in one block, they are both considered to be in the same coal zone in this study. 'Marine zone' indicates the presence of an unnamed marine zone. Boxes are not to scale and do not imply length of time, thickness of interval, or aerial extent of unit. 'Group (this report)' indicates stratigraphic group names used throughout the northern and central Appalachian Basin coal resource assessment reports for data entry purposes. 'Code (this report)' indicates code used in this chapter for data entry purposes. 'SGB' is selenium greater than background interval from table 2. Stratigraphic position and correlative coal beds are indicated for Pond Creek coal and Coalburg coal bed (see fig. 3). Pittsburgh coal bed (see fig. 3) is in the Upper Pennsylvanian Monongahela Formation, which is above the stratigraphic interval in this figure.

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System	Series	Midcontinent Stage	Group (this report)	Code (this report)	Coal Zone Names (this report)	Formation	Formal or informal units	Formation	Divisions of Blake (1998)	Pennsylvania	West Virginia	
											Kanawha Valley region	Tug Fork region	
							Bituminous coal field			Southern West Virginia coal field	Southern West Virginia coal field	Southern West Virginia coal field
										Boone, Clay, Fayette, Greenbrier, Kanawha, Nicholas, Raleigh, Wyoming Cos.	Boone, Lincoln, Logan, McDowell, Mingo, Wayne, Wyoming Cos.	
					Coal Zone Names (this report)		Formal or informal units			Formal or informal units	Formal or informal units	Formal or informal units
		Desmoinesian (part)	Allegheny (part)			Allegheny (part)	Lower Kittanning coal	Charleston Sandstone (part)		No. 6 Block coal (a,b,c)	No. 6 Block coal (a,b,c)	No. 6 Block coal zone (a,b,c)
				13	No. 5 Block coal zone		Clarion coal (?)			No. 5 Block coal (a,b,c)	No. 5 Block coal (a,b,c)	No. 5 Block coal zone (a,b,c)
							Brookville coal (?)			Little No. 5 Block coal (c)	Little No. 5 Block coal (c)	Little No. 5 Block coal (c)
										Stockton "A" coal (c)	Stockton "A" coal (c)	Stockton "A" coal (c)
		Atokan					Homewood Sandstone Member		upper	Kanawha black flint of White (1891)	Kanawha black flint of White (1891)	Kanawha black flint of White (1891)
				14	Stockton and Coalburg coal zone		Lower Mercer coal (?)			Stockton coal	Stockton coal	Stockton coal zone (c,d)
				15						Coalburg coal	Coalburg coal	Coalburg coal zone (c,d)
										Arnett Member (d)	Arnett Member (d)	Arnett Member (d)
				16	Winifrede/Hazard coal zone					Winifrede coal (d,e)	Winifrede, Buffalo Creek coals (d,e)	Winifrede coal zone (c,d,f)
				17						Lower Winifrede coal (d,e)	Lower Winifrede, Lower Buffalo Creek coals (d,e)	
										Winifrede limestone of White (1908) (c,d,f)	Buffalo Creek limestone of Hennen and Reger (1914) (c,d,f)	Winifrede Shale Member (c,d,f)

Group as used by Chesnut (1992)	Formations of Chesnut (1992)	Kentucky		Formation	Informal division of Nolde (1994a)	Virginia	Formation of Wilson and others (1956) as revised by Hardeman and others (1966)	Tennessee		SGB interval (from table 2)	Coal bed (from fig. 3)
			Harlan subdistrict					Jellico area	Walnut Mountain area		
		Hazard and Big Sandy reserve districts	Upper Cumberland River reserve district								
		Eastern Kentucky coal field	Eastern Kentucky coal field			Southwest Virginia coal field		west of Cumberland overthrust sheet	Cumberland overthrust sheet		
		Breathitt, Floyd, Harlan, Johnson, Knott, Leslie, Letcher, Martin, Perry, Pike Cos.	Bell, Harlan, Letcher Cos.			western Buchanan, Dickenson, Lee, Wise Cos.		Anderson, Campbell, Morgan, Scott Cos.	Campbell, Claiborne Cos.	SGB interval (from table 2)	Coal bed (from fig. 3)
		Formal or informal units	Formal or informal units	Formation		Formal or informal units		Formal or informal units	Formal or informal units		
Princess (part)		eroded	eroded	Harlan		eroded		eroded	eroded	post-SGB interval (part) (from table 2)	
		Richardson, Skyline coal zones (g,h)									
		Stoney Fork Member (?) (g)									
Four Corners		Broas coal zone (e,g,h)	Black Mountain coal zone (h)			No. 13 coal	Vowell Mountain (part)				
		Peach Orchard coal zone (e,g,h)	High Splint coal zone (h)		age of Atokan Age	High Splint coal (i)		Hazard No. 9 (?) (k)	eroded	SGB interval (from table 2)	Coalburg coal (from fig 3)
		Arnett Member (h)									
		Hazard coal zone (h)	Morris coal zone (h)			Morris, No. 11 coals (i,j)	oak Mountain	Braden Mountain, Pewee coals (l)			
		Haddix coal zone (h)	Lower Highsplint coal (h)					Red Ash coal			
			Reynolds Sandstone Member (h)			Reynolds Sandstone Member (i,j)		Fodderstack Sandstone Member			
		Magoffin Member (g,h)	Magoffin Member (g,h)			Magoffin Member		Magoffin Member			

System	Series	Midcontinent Stage	Group (this report)	Code (this report)	Coal Zone Names (this report)	Formation	Formal or informal units (Pennsylvania — Bituminous coal field)	Formation	Divisions of Blake (1998)	Formal or informal units (Kanawha Valley region — Southern West Virginia coal field — Boone, Clay, Fayette, Greenbrier, Kanawha, Nicholas, Raleigh, Wyoming Cos.)	Formal or informal units (Tug Fork region — Southern West Virginia coal field — Boone, Lincoln, Logan, McDowell, Mingo, Wayne, Wyoming Cos.)	Formal or informal units (Southern West Virginia coal field)
Pennsylvanian (part)	Middle (part)	Morrowan (part)	Pottsville (part)			Pottsville (part)	?	Kanawha Formation (part)	middle	Chilton coal (c,d,f)	Chilton "A" coal (c,d,f)	Chilton coal zone (c,d,f)
												marine zone (d)
										Hernshaw coal (?) (c,d,f)	Chilton coal (c,f)	Fire Clay coal zone (c,d,f)
										Seth limestone of Krebs and Teets (1915) (c,d,f)		marine zone (c,d,f)
										Cedar Grove coal (c,d,f)	Hernshaw coal (c,d,f)	Cedar Grove coal (d.f)
											Dingess limestone of Hennen and Reger (1914) (c,d,f)	Dingess Shale Member
				22	Williamson/Amburgy coal zone					Alma coal (c,d,f)	Williamson coal (c,d,f)	Williamson coal zone
										Campbell Creek limestone of White (1885) (c,d,f)	Seth limestone of Krebs and Teets (1915) (d)	Campbell Creek limestone of White (1885)
				24	Campbell Creek/Upper Elkhorn No. 3 coal zone					Peerless coal, Campbell Creek coal zone (c,d,f)	Cedar Grove coal (c,d,f)	Peerless, Campbell Creek coal zones (c,f)
										No. 2 Gas, Campbell Creek coal zone (c,d,f)	Lower Cedar Grove coal (c,d,f)	No. 2 Gas, Campbell Creek coal zones (c,d,f)
				25	Upper Elkhorn Nos. 1 and 2/Powellton coal zone					Powellton coal (c,d,f)	Alma coal (c,d,f)	Powellton coal zone (d)
										Cannelton limestone of White (1885) (c,d,f)	Campbell Creek limestone of White (1885) (c,d,f)	Crummies Member (d)
										Eagle coal (c,d,f)	Campbell Creek coal (c,f)	Eagle coal zone (c,d)
										Eagle limestone and shale of White (1891) (c,d,f)	Cannelton limestone of White (1885) (c,d,f)	Betsie Shale Member

modified from Neuzil (2001) U.S. Geological Survey Professional Paper 1625-C, Chapter I, Figure 1.

		Kentucky		Virginia			Tennessee				
		Hazard and Big Sandy reserve districts	Harlan subdistrict / Upper Cumberland River reserve district					Jellico area	Walnut Mountain area		
		Eastern Kentucky coal field	Eastern Kentucky coal field			Southwest Virginia coal field		west of Cumberland overthrust sheet	Cumberland overthrust sheet		
		Breathitt, Floyd, Harlan, Johnson, Knott, Leslie, Letcher, Martin, Perry, Pike Cos.	Bell, Harlan, Letcher Cos.			western Buchanan, Dickenson, Lee, Wise Cos.		Anderson, Campbell, Morgan, Scott Cos.	Campbell, Claiborne Cos.	SGB interval (from table 2)	Coal bed (from fig. 3)
Group as used by Chesnut (1992)	Formations of Chesnut (1992)	Formal or informal units	Formal or informal units	Formation	Informal division of Nolde (1994a)	Formal or informal units	Formation of Wilson and others (1956) as revised by Hardeman and others (1966)	Formal or informal units	Formal or informal units		
Breathitt (part)	Hyden	Copland coal zone, Taylor coal	Limestone coal	Wise (part)	Wis…	Pardee coal	Red…	Sharp coal			
		marine zone (h)	marine zone (h)					Caryville Sandstone Member (?)			
		Fire Clay rider coal zone	Smith coal zone			Gin Creek coal		Big Mary coal			
		Fire Clay coal	Wallins Creek coal zone		unit 3	Phillips coal	Graves Gap	Windrock coal	Walnut Mountain coal		
		member J (h)						Roach Creek Sandstone Member (?)	Magoffin Member (l)		
		Whitesburg coal zone	Stray coal zone			House coal (?) (i,j)		Upper Pioneer coal			
		Kendrick Shale Member (g,h)	Kendrick Shale Member (g,h)			Kendrick Shale Member		Kendrick Shale Member			
	Pikeville	Williamson, Amburgy coal zones	Creech coal zone			Low Splint coal	Indian Bluff	Lower Pioneer, Jordan coals	Windrock coal (l)		
		Elkins Fork shale of Morse (1931) (h)	Elkins Fork shale of Morse (1931) (h)		unit 2	Marcum Hollow Sandstone Member		Pioneer Sandstone Member			
		Upper Elkhorn No. 3 coal zone	Taggart coal zone (h)			Taggart coal (i,j)		Elk Gap coal	Jordan coal (l)		
			Taggart Marker coal (h)			Taggart Marker coal (i,j)			Pioneer Sandstone Member (?) (l)	pre-SGB interval (part) (from table 2)	
		Upper Elkhorn No. 1, Upper Elkhorn No. 2 coals (h)	Harlan coal zone (h)			Wilson, Upper St. Charles coals (i,j)	Slatestone (part)	Jellico coal zone	Jellico coal zone (l)		
		Crummies Member (h)	Crummies Member (h)			marine zone (j)		Sand Gap Sandstone Member	Newcomb Sandstone Member		
		Pond Creek, Lower Elkhorn coals	Imboden coal, Path Fork coal zone (h)			Kelly coal, Imboden coal zone (i,j)		Blue Gem coal zone	Rich Mountain coal zone		Pond Creek coal (from fig 3)
		Betsie Shale Member (g,h)	Betsie Shale Member (g,h)			Betsie Shale Member (j)		Betsie Shale Member	Betsie Shale Member		

Figure 3a. Histograms of selenium concentration in three coal beds (Pond Creek, Coalburg, and Pittsburgh) that each have > 100 samples.

Histogram of selenium concentration in three coal beds

Percent of samples — Se (ppm remnant-moisture, whole-coal)

☐ Pond Creek ☐ Coalburg ☐ Pittsburgh
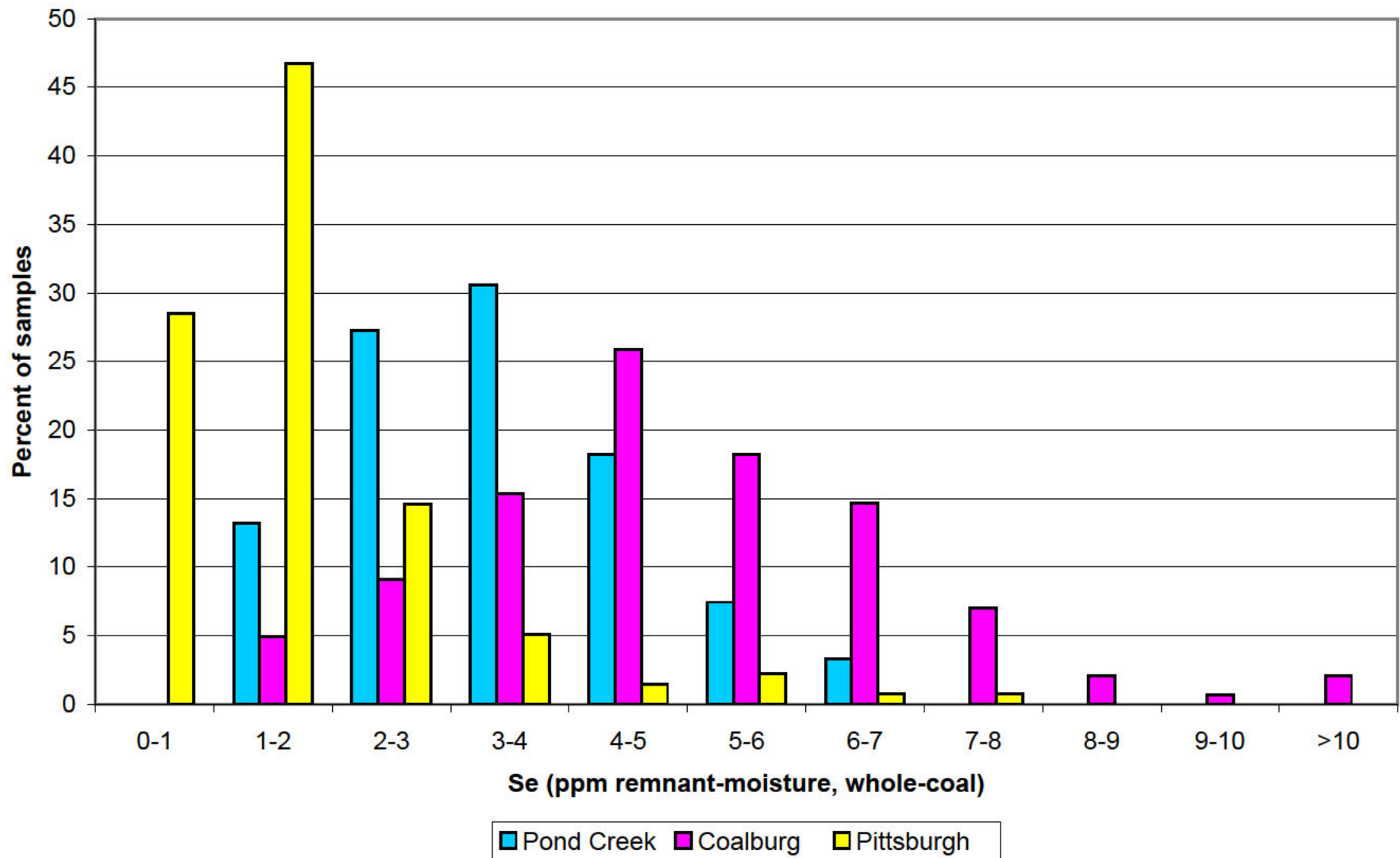
Figure3b. Histograms of ash yield concentration in three coal beds (Pond Creek, Coalburg, and Pittsburgh) that each have > 100 samples.

Histogram of ash yield in three coal beds

Ash yield (percent as-received, whole-coal)

Percent of samples

■ Pond Creek ■ Coalburg □ Pittsburgh
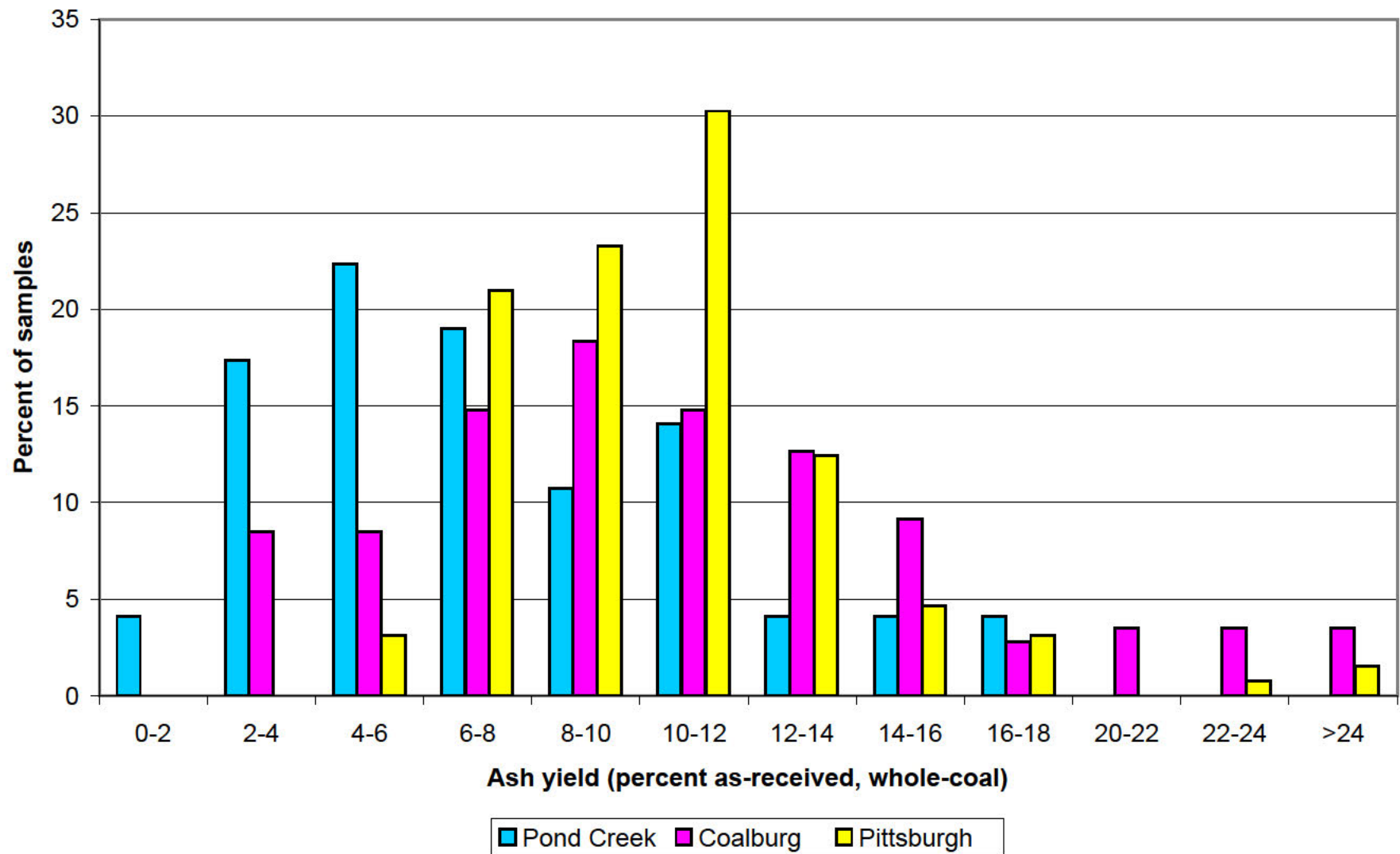
Figure 3c. Histograms of sulfur concentration in three coal beds (Pond Creek, Coalburg, and Pittsburgh) that each have > 100 samples.

Histogram of sulfur concentration in three coal beds
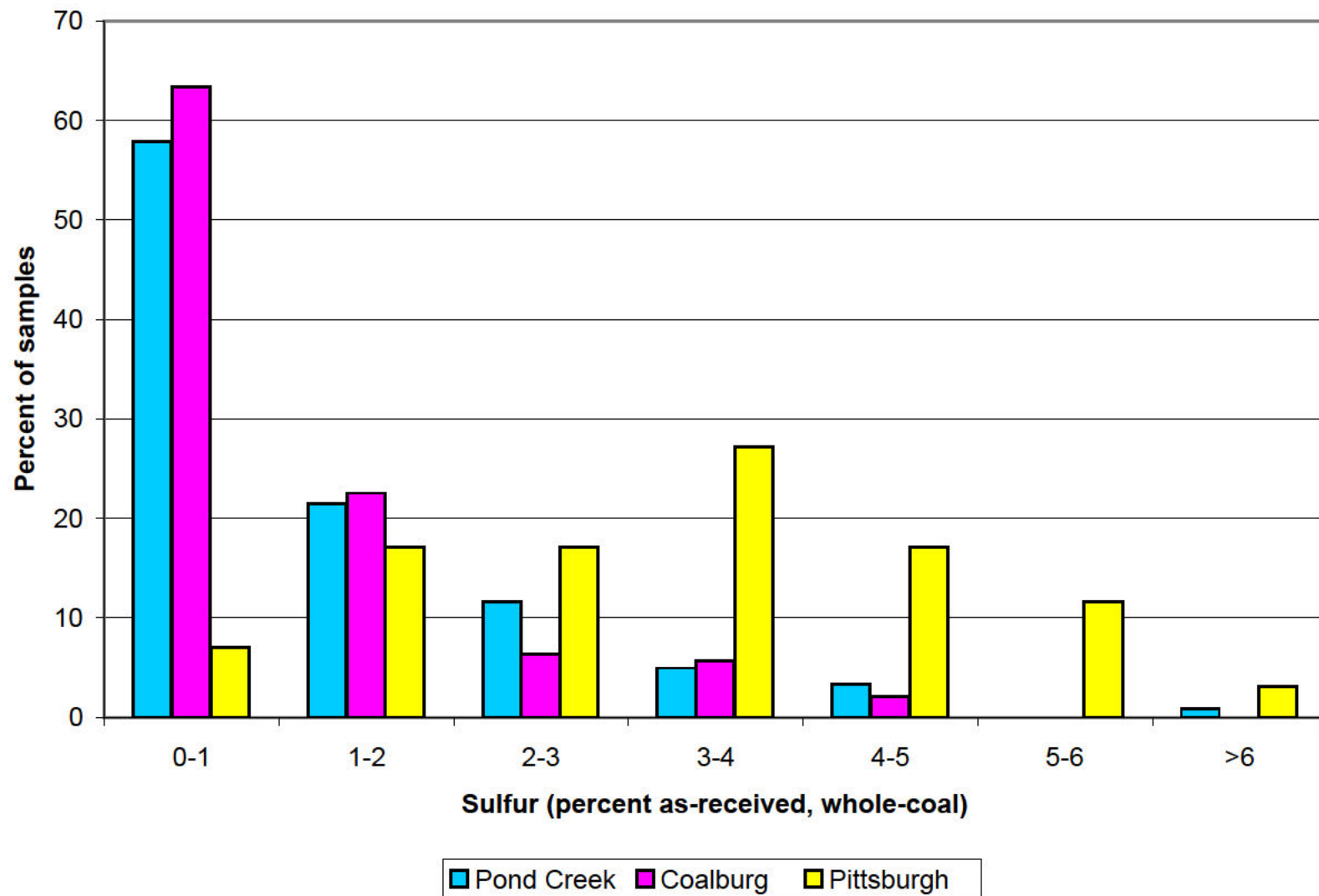
Figure 4a. Chart of average, median, and geometric mean of selenium concentration in coal beds with $\geq$ 30 samples.

Se (ppm remnant-moisture, whole-coal)

coal bed (≥30 samples)

◆ Geometric Mean □ Median △ Average
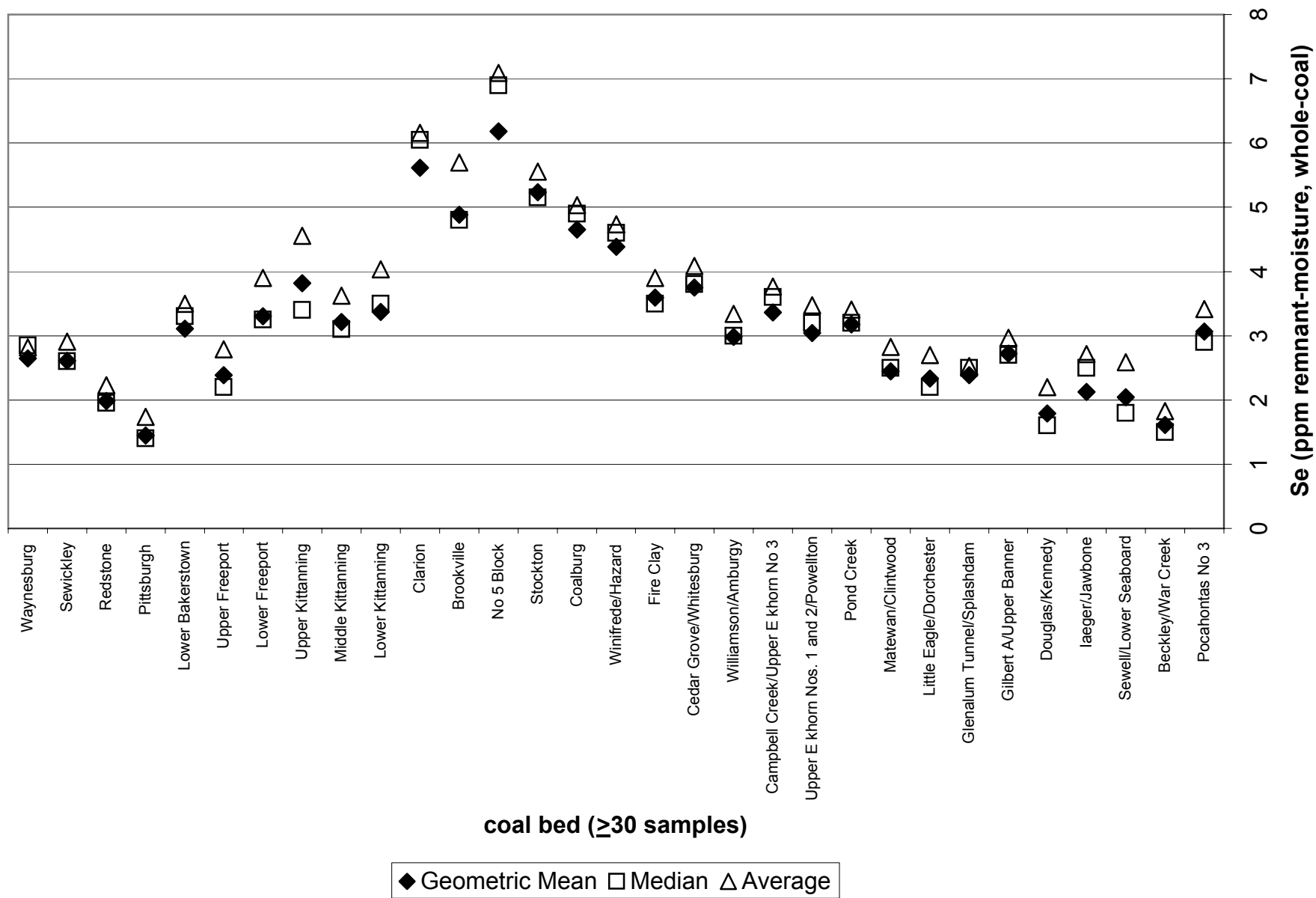
Figure 4b. Chart of average, median, and geometric mean of ash yield in coal beds with $\geq$ 30 samples.

Ash yield (percent as-received, whole-coal)

coal beds ≥30 samples

◆ Geo Mean ☐ Median △ Arith Mean

X-axis labels: Waynesburg, Sewickley, Redstone, Pittsburgh, Lower Bakerstown, Upper Freeport, Lower Freeport, Upper Kittanning, Middle Kittanning, Lower Kittanning, Clarion, Brookville, No 5 Block, Stockton, Coalburg, Winifrede/Hazard, Fire Clay, Cedar Grove/Whitesburg, Williamson/Amburgy, Campbell Creek/Upper E khorn No 3, Upper E khorn Nos. 1 and 2/Powellton, Pond Creek, Matewan/Clintwood, Little Eagle/Dorchester, Glenalum Tunnel/Splashdam, Gilbert A/Upper Banner, Douglas/Kennedy, Iaeger/Jawbone, Sewell/Lower Seaboard, Beckley/War Creek, Pocahontas No 3

Figure 4c. Chart of average, median, and geometric mean of sulfur concentration in coal beds with $\geq$ 30 samples.

Sulfur (percent as-received, whole-coal)

coal beds ≥30 samples

◆ Geo Mean ☐ Median △ Arith Mean
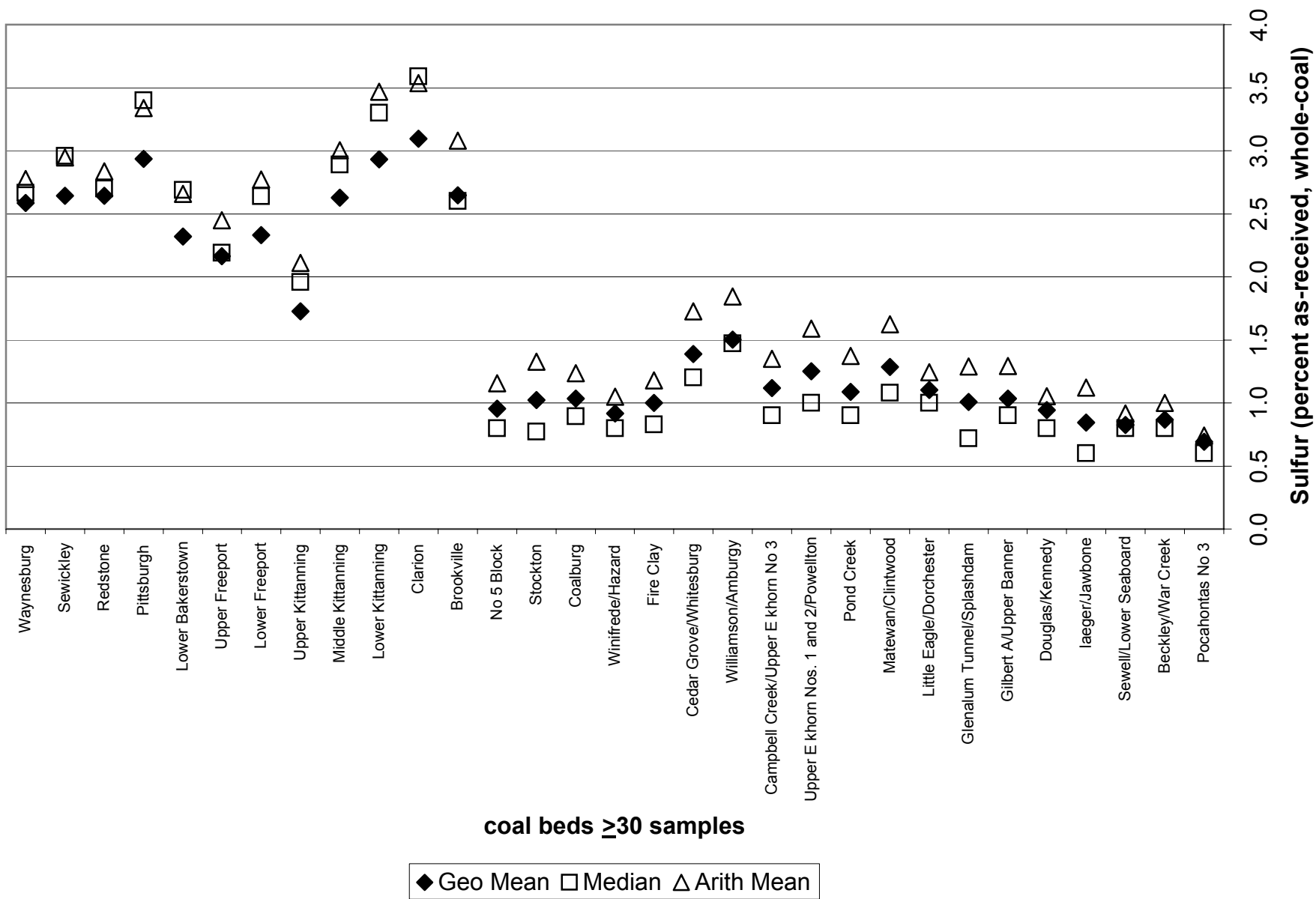
Figure 5a. Chart of median and midspread of selenium concentration in coal beds with $\geq$ 30 samples.
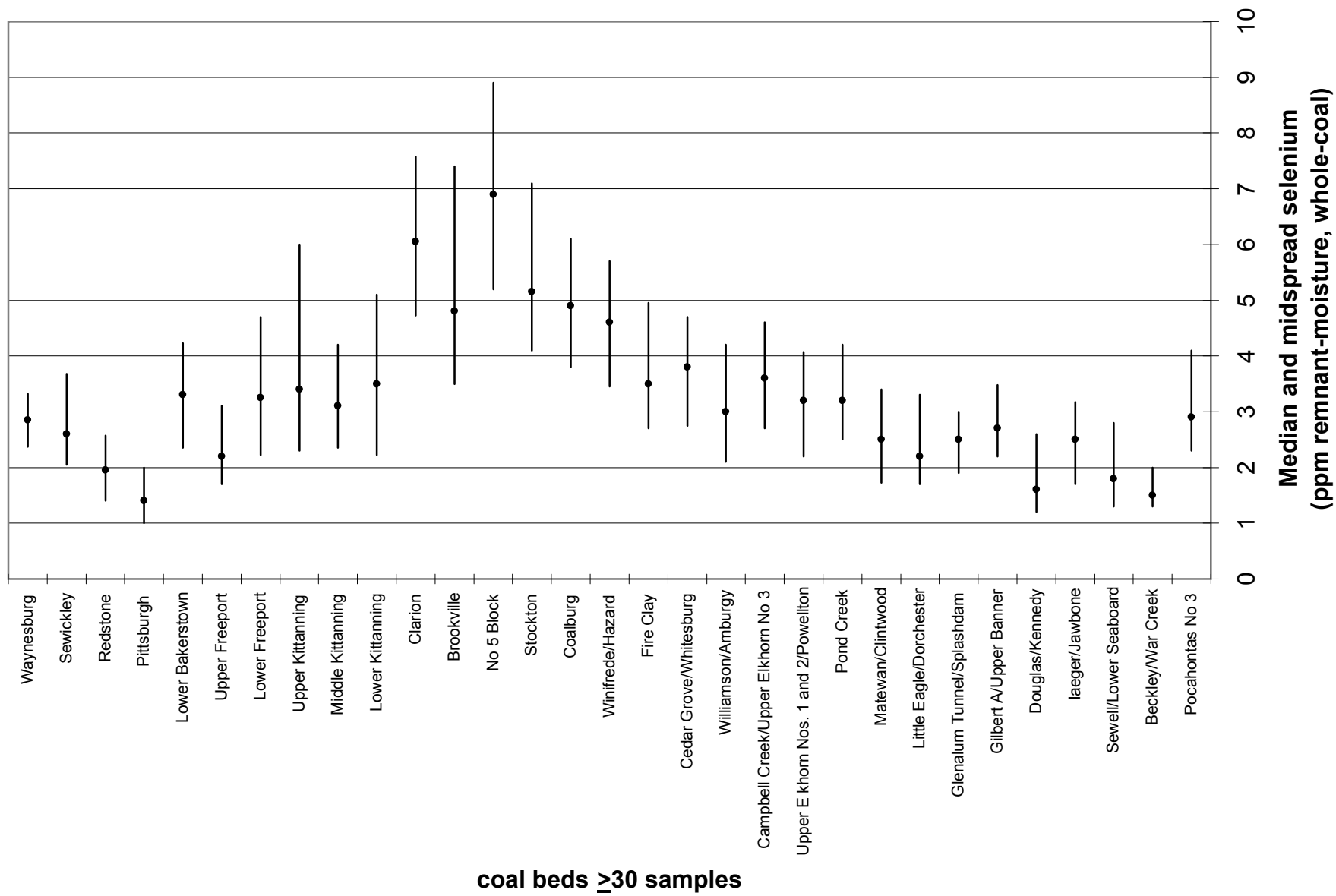
Figure 5b. Chart of median and midspread of ash yield in coal beds with $\geq$ 30 samples.
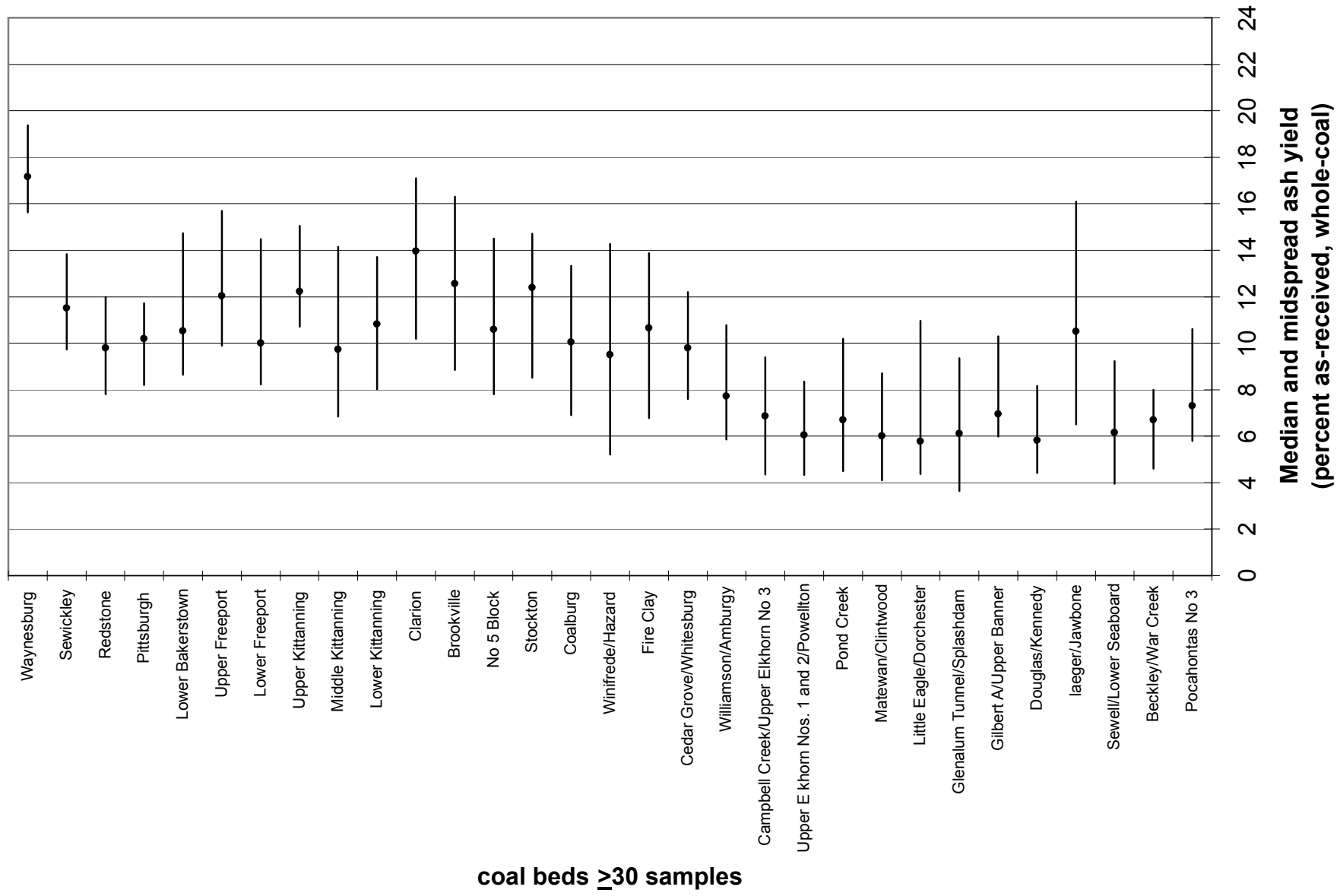
Figure 5c. Chart of median and midspread of sulfur concentration in coal beds with ≥ 30 samples.

coal beds ≥30 samples

Median and midspread sulfur (percent as-received, whole-coal)

Waynesburg
Sewickley
Redstone
Pittsburgh
Lower Bakerstown
Upper Freeport
Lower Freeport
Upper Kittanning
Middle Kittanning
Lower Kittanning
Clarion
Brookville
No 5 Block
Stockton
Coalburg
Winifrede/Hazard
Fire Clay
Cedar Grove/Whitesburg
Williamson/Amburgy
Campbell Creek/Upper Elkhorn No 3
Upper E khorn Nos. 1 and 2/Powellton
Pond Creek
Matewan/Clintwood
Little Eagle/Dorchester
Glenalum Tunnel/Splashdam
Gilbert A/Upper Banner
Douglas/Kennedy
Iaeger/Jawbone
Sewell/Lower Seaboard
Beckley/War Creek
Pocahontas No 3

Figure 6a. Chart of geometric mean of selenium concentration for all, thick ($\geq$ 28 inch), or thin ($<$ 28 inch) coal samples in coal beds with $\geq$ 30 samples.

coal beds ≥30 samples

◆ All   □ >28 inch   △ <28 inch

Geometric mean selenium
(ppm remnant-moisture, whole-coal)

Waynesburg
Sewickley
Redstone
Pittsburgh
Lower Bakerstown
Upper Freeport
Lower Freeport
Upper Kittanning
Middle Kittanning
Lower Kittanning
Clarion
Brookville
No 5 Block
Stockton
Coalburg
Winifrede/Hazard
Fire Clay
Cedar Grove/Whitesburg
Williamson/Amburgy
Campbell Creek/Upper Elkhorn No 3
Upper Elkhorn Nos. 1 and 2/Powellton
Pond Creek
Matewan/Clintwood
Little Eagle/Dorchester
Glenalum Tunnel/Splashdam
Gilbert A/Upper Banner
Douglas/Kennedy
Iaeger/Jawbone
Sewell/Lower Seaboard
Beckley/War Creek
Pocahontas No 3

Figure 6b. Chart of geometric mean of ash yield for all, thick ($\geq$ 28 inch), or thin ($<$ 28 inch) coal samples in coal beds with $\geq$ 30 samples.

Geometric mean ash yield (percent as-received, whole-coal)

coal beds ≥30 samples

◆ All □ >28 inch △ <28 inch
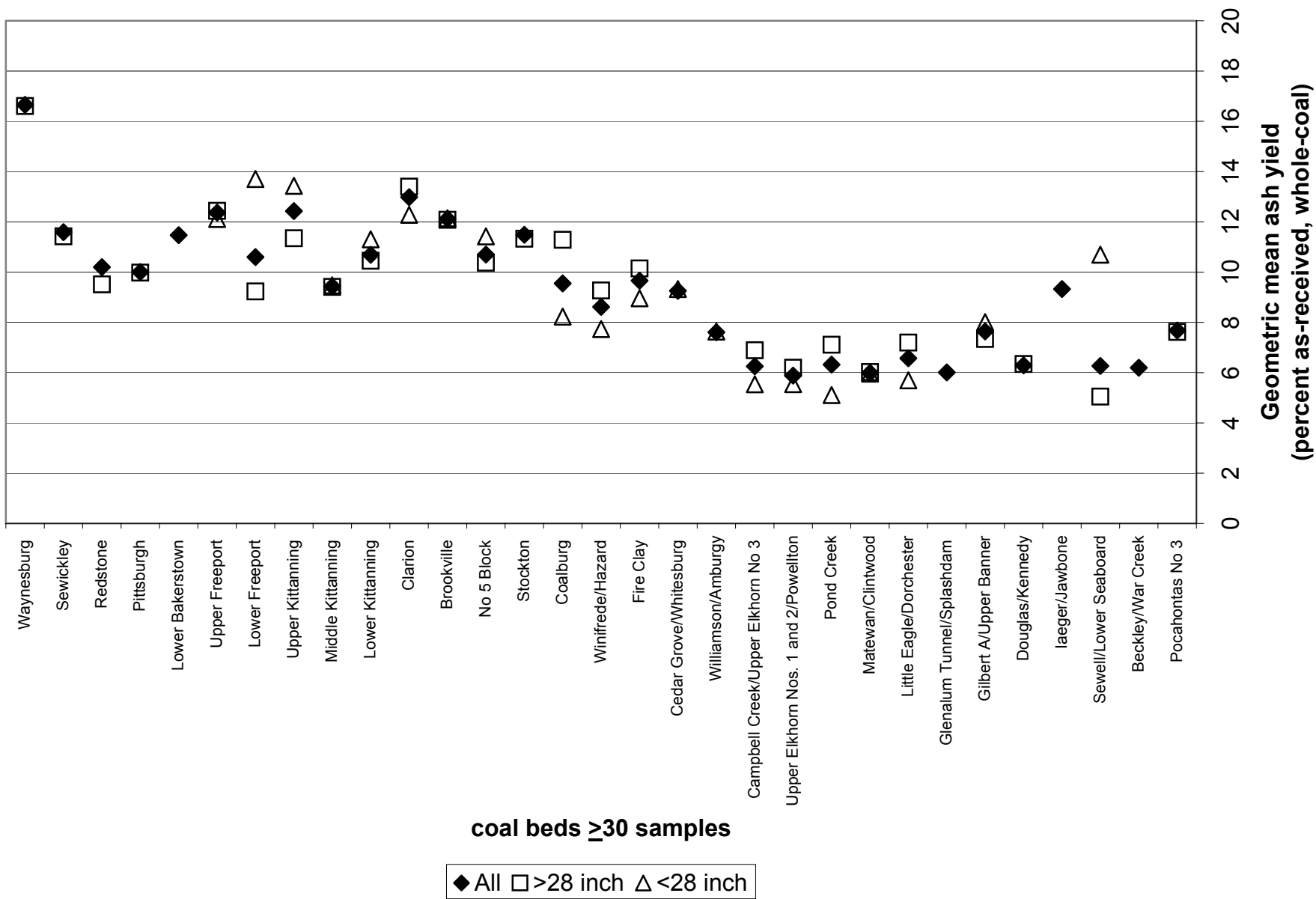
Figure 6c. Chart of geometric mean of sulfur concentration for all, thick ($\geq$ 28 inch), or thin ($<$ 28 inch) coal samples in coal beds with $\geq$ 30 samples.

coal beds ≥30 samples

Geometric mean sulfur (percent as-received, whole-coal)

◆ All ☐ >28 inch △ <28 inch
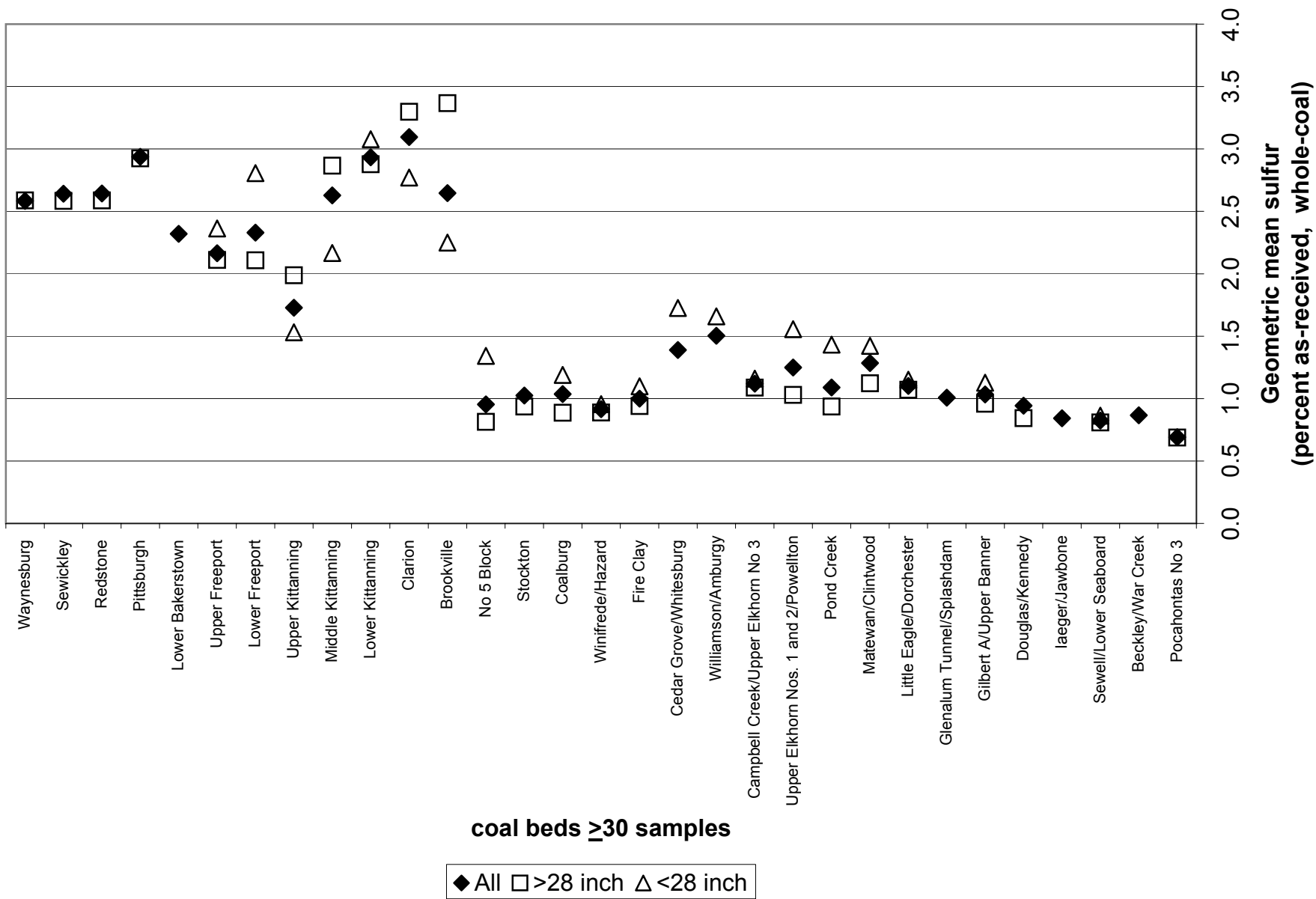
Figure 7a. Histograms of selenium, ash yield and sulfur concentrations in three stratigraphic intervals (pre-SGB, SGB, and post-SGB) for all coal bed samples. [Number of samples listed in table 5a. Coal beds in stratigraphic intervals pre-SGB, SGB, and post-SGB listed in table 2.]

Histogram of selenium concentration in three stratigraphic intervals for all coal bed samples.

Histogram of ash yield in three stratigraphic intervals for all coal bed samples.

percent of samples

Ash yield range (percent as-received, whole-coal)
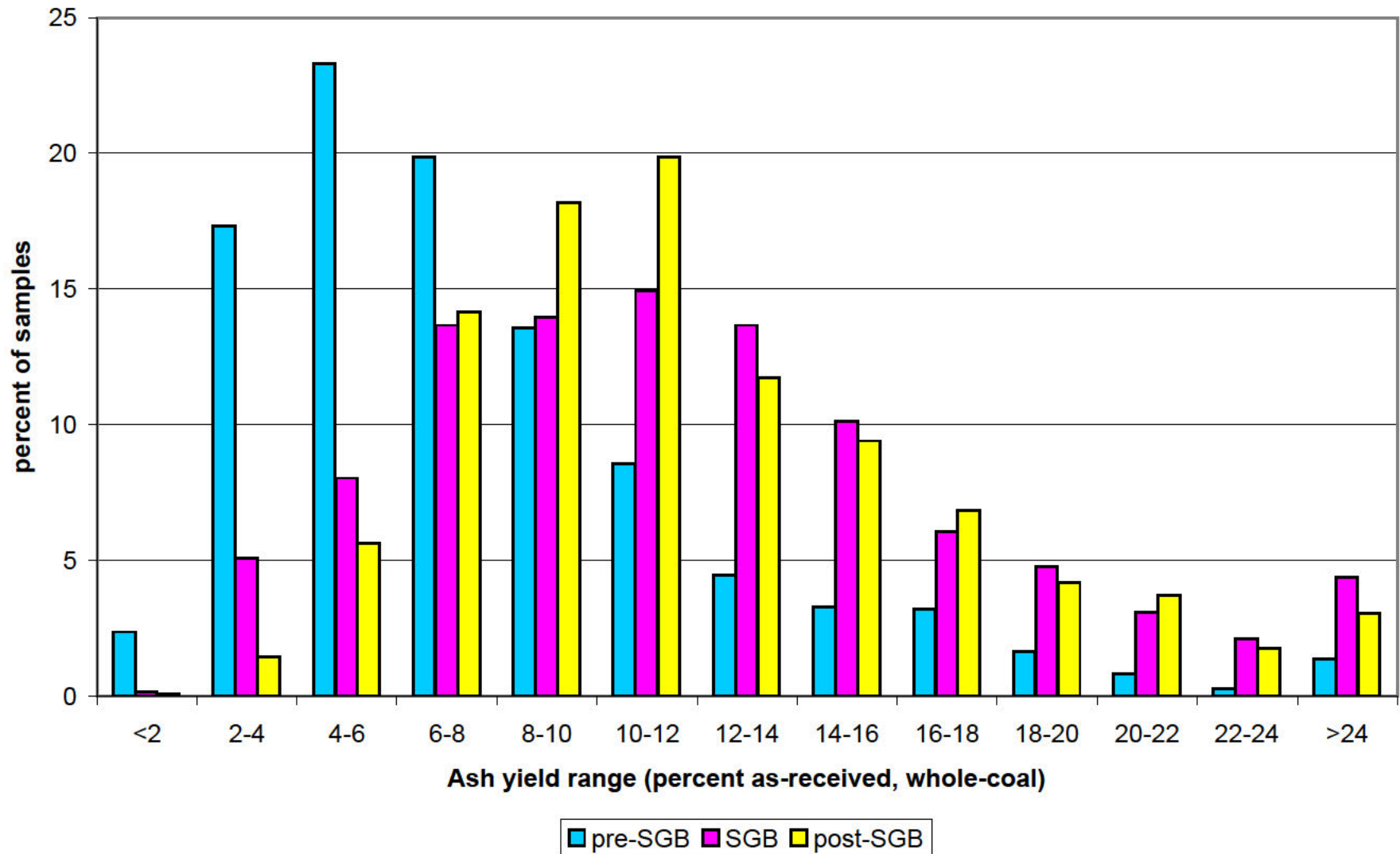
□ pre-SGB ■ SGB □ post-SGB

Histogram of total sulfur concentration in three stratigraphic intervals for all coal bed samples.
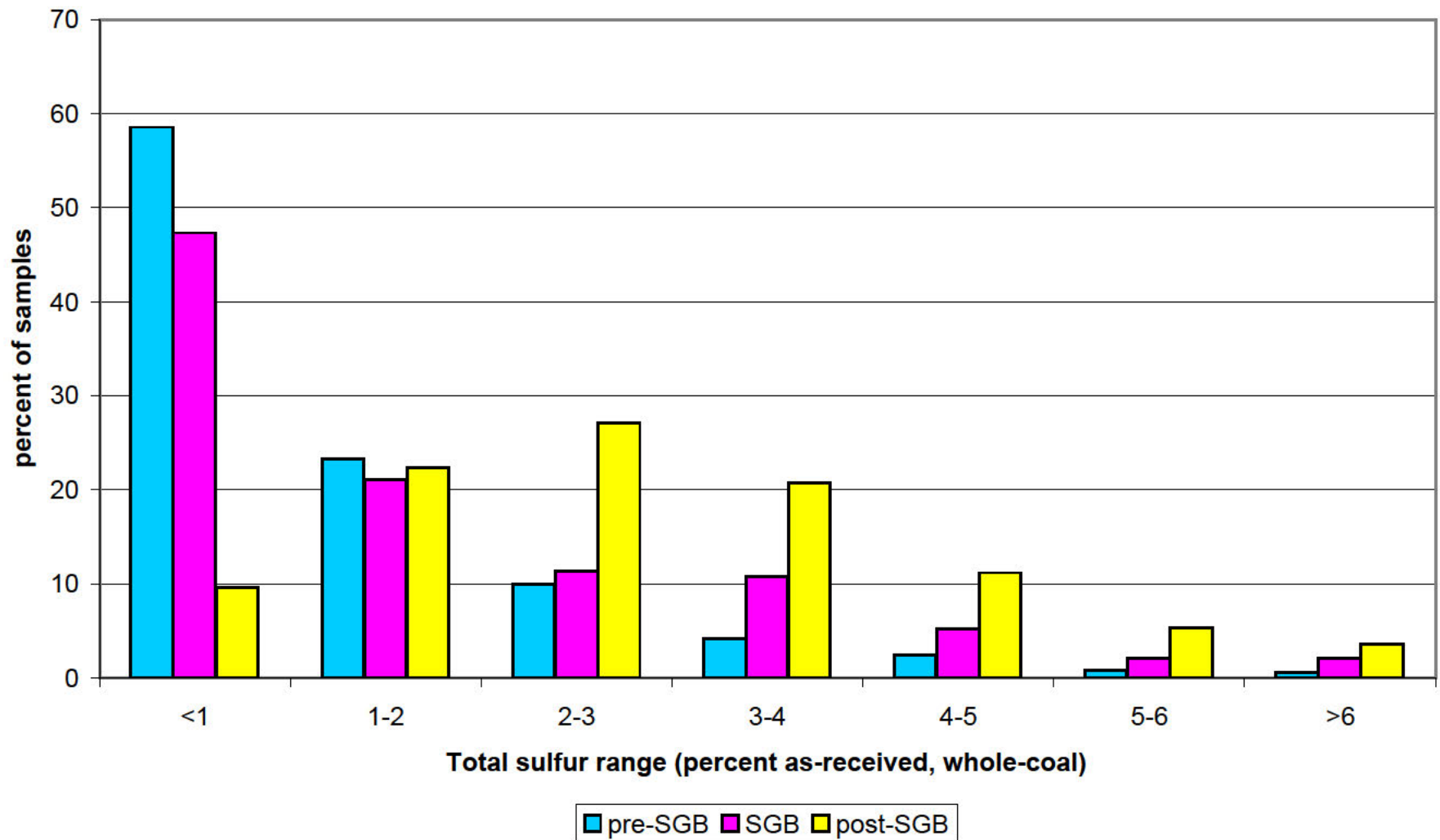
Figure 7b. Histograms of selenium, ash yield and sulfur concentrations in three stratigraphic intervals (pre-SGB, SGB, and post-SGB) for thick ($\geq$ 28 inch) coal bed samples. [Number of samples listed in table 5b. Coal beds in stratigraphic intervals pre-SGB, SGB, and post-SGB listed in table 2.]

Histogram of selenium concentration in three stratigraphic intervals for thick (≥28 inch) coal bed samples.
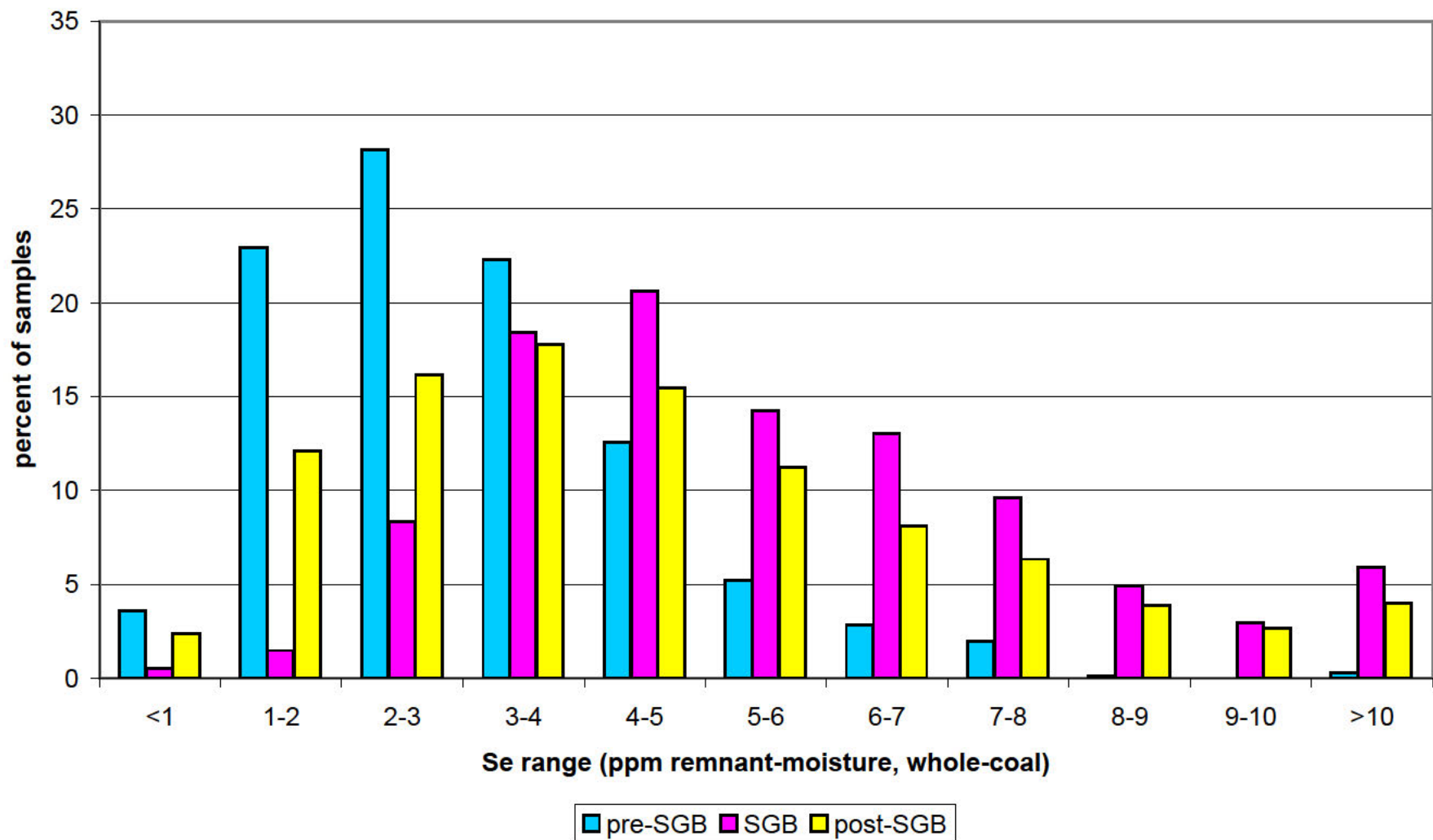
Histogram of ash yield in three stratigraphic intervals for thick (≥28 inch) coal bed samples.
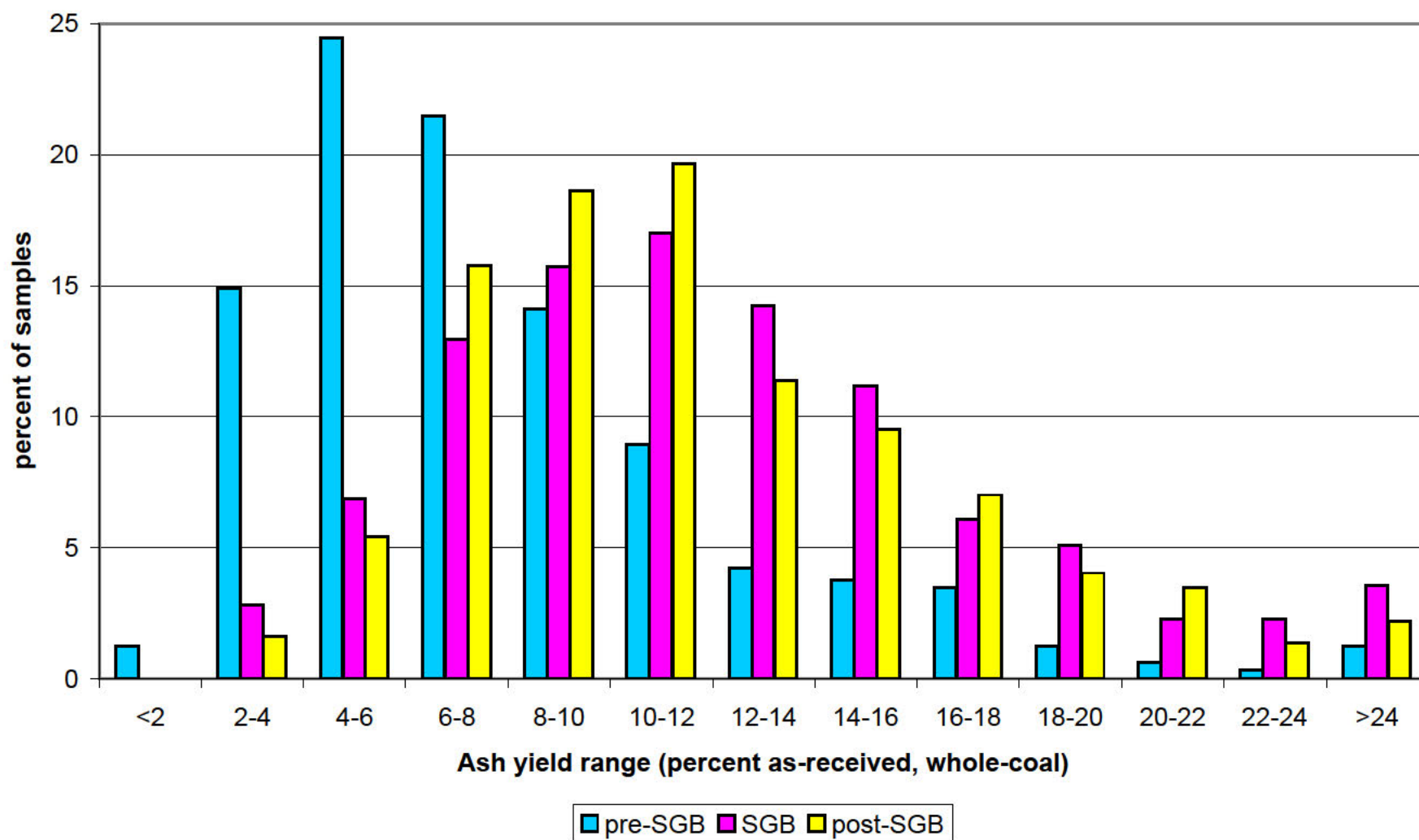
Histogram of total sulfur concentration in three stratigraphic intervals for thick (≥28 inch) coal bed samples.
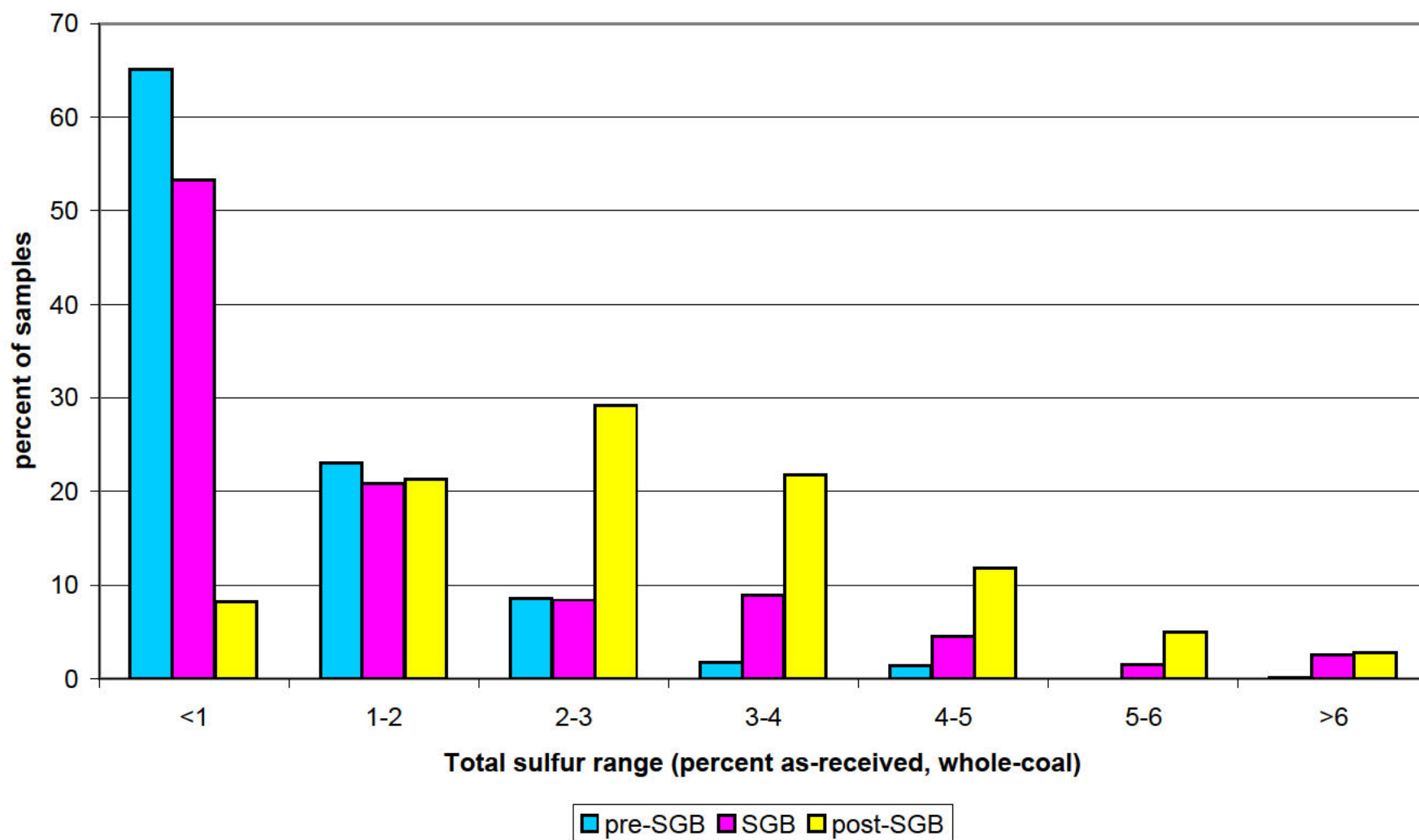
Figure 7c. Histograms of selenium, ash yield and sulfur concentrations in three stratigraphic intervals (pre-SGB, SGB, and post-SGB) for thin (< 28 inch) coal bed samples. [Number of samples listed in table 5c. Coal beds in stratigraphic intervals pre-SGB, SGB, and post-SGB listed in table 2.]

Histogram of selenium concentration in three stratigraphic intervals for thin (<28 inch) coal bed samples.

percent of sample

Se range (ppm remnant-moisture, whole-coal)

☐ pre-SGB ☐ SGB ☐ post-SGB

Histogram of ash yield in three stratigraphic intervals for thin (<28 inch) coal bed samples.

Histogram of total sulfur concentration in three stratigraphic intervals for thin (<28 inch) coal bed samples.

Total sulfur range (percent as-received, whole-coal)

percent of samples

■ pre-SGB ■ SGB □ post-SGB

COAL BED NAMES (COALQUAL database)			Number of Samples						
COAL BED NAMES (BOLD, THIS REPORT)	**PA**	**MD**	**OH**	**nWV**	**sWV**	**KY**	**TN**	**VA**	**Total**
WAYNESBURG	29	1		6					36
WAYNESBURG NO 11			24						24
WAYNESBURG	**29**	**1**	**24**	**6**					**60**
MEIGS CREEK NO 9			27						27
SEWICKLEY	11	2		2					15
SEWICKLEY	**11**	**2**	**27**	**2**					**42**
FISHPOT	**1**		**3**						**4**
REDSTONE	14	1		42					57
REDSTONE NO 8A			17						17
REDSTONE	**14**	**1**	**17**	**42**					**74**
PITTSBURGH ROOF	8								8
PITTSBURGH ROOSTER	2								2
PITTSBURGH ROOF	**10**								**10**
PITTSBURGH	29	1		40					70
PITTSBURGH NO 8			66						66
PITTSBURGH-PITTSBURGH ROOF	1								1
PITTSBURGH	**30**	**1**	**66**	**40**					**137**
ELK LICK				1					1
WELLERSBURG	2								2
ELK LICK	**2**			**1**					**3**
FEDERAL HILL	**3**								**3**
HARLEM	**1**	**3**	**5**						**9**
UPPER BAKERSTOWN	**4**								**4**
ANDERSON			11						11
BAKERSTOWN	1	3		1					5
BARTON	1								1
LOWER BAKERSTOWN	8	5							13
LOWER BAKERSTOWN	**10**	**8**	**11**	**1**					**30**
WILGUS			**4**						**4**
BRUSH CREEK	**9**	**2**							**11**
MAHON NG	7		11						18
SPEER	2								2
MAHONING	**9**		**11**						**20**
KELLY R DER	1								1
UPPER FREEPORT RIDER	5								5
UPPER FREEPORT RIDER	**6**								**6**
KELLY	1								1
PR NCESS NO 9				4		1			5
UPPER FREEPORT	192	20		3					215
UPPER FREEPORT NO 7			57						57
UPPER FREEPORT	**193**	**20**	**57**	**7**		**1**			**278**
LOWER FREEPORT	57								57
LOWER FREEPORT NO 6A			42						42
LOWER FREEPORT R DER	1								1
MOSHANNON	2								2
PR NCESS NO 8						1			1
LOWER FREEPORT	**60**		**42**			**1**			**103**
UPPER KITTANNING 2 RIDER	1								1
UPPER KITTANNING R DER	2								2
UPPER KITTANNING RIDER	**3**								**3**
UPPER KITTANNING	**64**	**2**		**1**					**67**

Table 1. Coal bed names used in this report (names in bold), correlative alternate coal bed names used in COALQUAL database (see column CBED in Appendix 1), number of samples (N) from each state, and total number of samples for each coal bed (in bold) [nWV = northern West Virgina coal field sWV = southern West Virginia coal field]

COAL BED NAMES (COALQUAL database)	Number of Samples								
COAL BED NAMES (BOLD, THIS REPORT)	**PA**	**MD**	**OH**	**nWV**	**sWV**	**KY**	**TN**	**VA**	**Total**
M DDLE KITTANNING 1 RIDER	2								2
M DDLE KITTANNING 2 RIDER	2								2
M DDLE KITTANNING R DER	4								4
MIDDLE KITTANNING RIDER	**8**								**8**
M DDLE KITTANNING	78	2		3					83
M DDLE KITTANNING A	1								1
M DDLE KITTANNING NO 6			151						151
M DDLE KITTANNING SPLIT	1								1
PR NCESS NO 7						7			7
MIDDLE KITTANNING	**80**	**2**	**151**	**3**		**7**			**243**
STRASBURG	1								1
STRASBURG NO 5A			10						10
STRASBURG	**1**		**10**						**11**
LOWER KITTANN NG 1 R DER	2								2
LOWER KITTANN NG 2 R DER	2								2
LOWER KITTANN NG 3 R DER	1								1
LOWER KITTANN NG R DER	2								2
LOWER KITTANNING RIDER	**7**								**7**
KITTANN NG		2							2
LAWRENCE			1						1
LOWER KITTANN NG	78	2		4					84
LOWER KITTANN NG NO 5			103						103
NO 6 BLOCK				5					5
PR NCESS NO 6						2			2
UPPER KITTANNING				1					1
LOWER KITTANNINGNo. 6 BLOCK	**78**	**4**	**104**	**10**		**2**			**198**
CLARION	8								8
CLARION 4A-SCRUBGRASS			1						1
CLARION COAL ZONE			6						6
CLARION NO 1	2								2
CLARION NO 2	1								1
CLARION NO 4A			40						40
CLARION-BROOKVILLE	2								2
CLARION-BROOKVILLE RIDER	1								1
LAUREL						1			1
LAUREL RIDER						1			1
SCRUBGRASS	2		4						6
UPPER CLARION	5								5
CLARION	**21**		**51**			**2**			**74**
BROOKV LLE	30								30
BROOKV LLE NO 4			30						30
BROOKV LLE-CLARION	2								2
LOWER CLARION	7								7
OGAN			1						1
WINTERS			3						3
BROOKVILLE	**39**		**34**						**73**

Table 1. Coal bed names used in this report (names in bold), correlative alternate coal bed names used in COALQUAL database (see column CBED in Appendix 1), number of samples (N) from each state, and total number of samples for each coal bed (in bold) [nWV = northern West Virgina coal field sWV = southern West Virginia coal field]

Table 1. Coal bed names used in this report (names in bold), correlative alternate coal bed names used in COALQUAL database (see column CBED in Appendix 1), number of samples (N) from each state, and total number of samples for each coal bed (in bold) [nWV = northern West Virgina coal field sWV = southern West Virginia coal field]

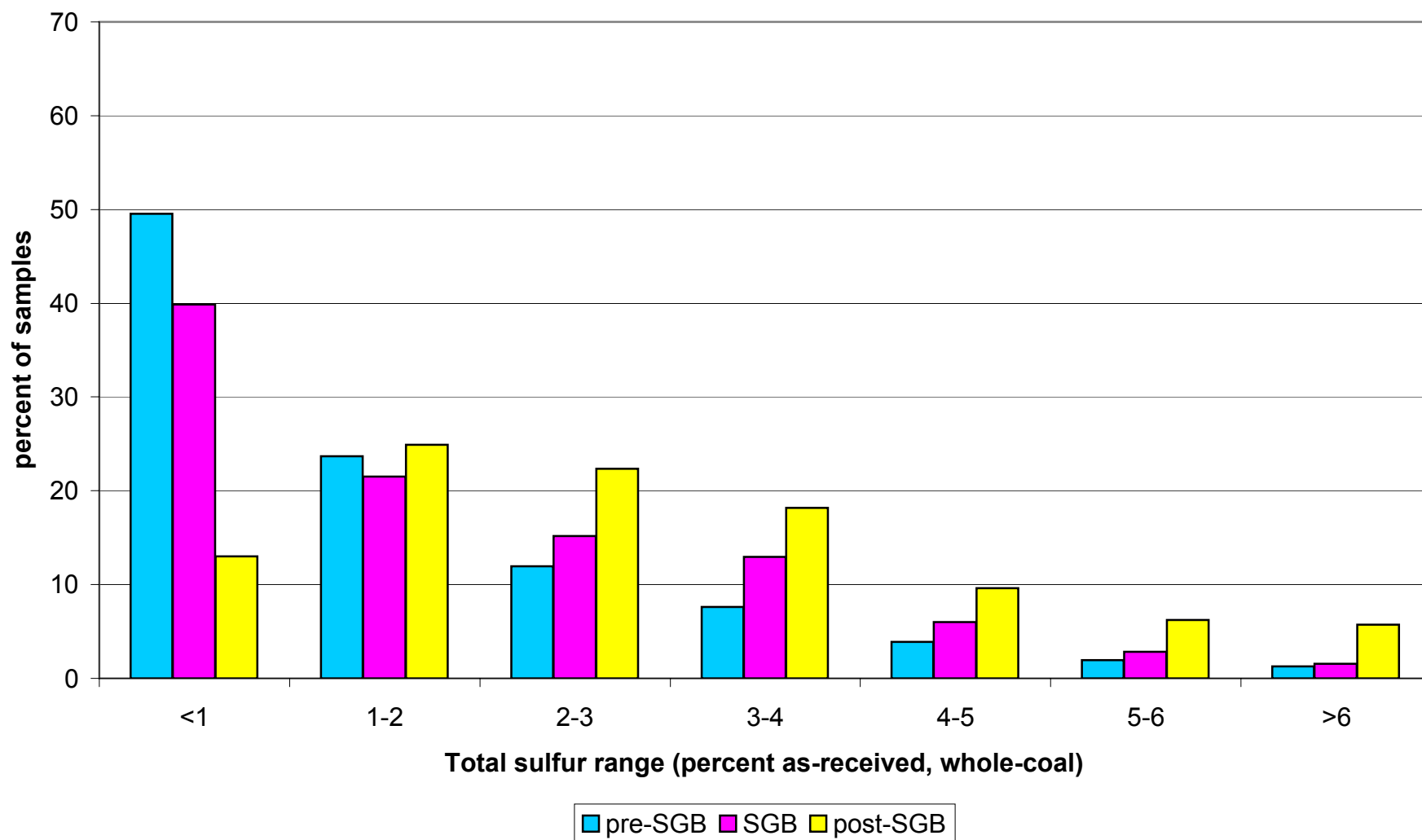| COAL BED NAMES (COALQUAL database)	Number of Samples								
COAL BED NAMES (BOLD, THIS REPORT)	PA	MD	OH	nWV	sWV	KY	TN	VA	Total
KNOB						1			1
KNOB SPLIT 2						1			1
KNOB ZONE						5			5
LOWER KITTANN NG					4				4
LOWER NO 5 BLOCK					6				6
LOWER RICHARDSON						1			1
NO 5 BLOCK					30				30
PR NCESS NO 5						5			5
RICHARDSON						19			19
RICHARDSON R DER						1			1
SKYLINE						8			8
SKYLINE SPLIT 1						1			1
SKYLINE SPLIT 2						1			1
SKYLINE SPLIT 3						1			1
SKYLINE SPLIT 4						1			1
SKYLINE SPLIT 5						1			1
SKYLINE SPLIT 6						1			1
UPPER NO 5 BLOCK					3				3
UPPER RICHARDSON						1			1
UPPER SPLIT NO 5 BLOCK					2				2
NO 5 BLOCK					**45**	**48**			**93**
STOCKTON A					3				3
UPPER KITTANNING					1				1
STOCKTON A/LITTLE NO 5 BLOCK					**4**				**4**
TIONESTA			**5**						**5**
UPPER MERCER	6								6
UPPER MERCER NO 3A			2						2
UPPER MERCER	**6**		**2**						**8**
LOWER MERCER	3								3
LOWER MERCER A	1								1
LOWER MERCER B	1								1
LOWER MERCER NO 3			2						2
MERCER	17								17
LOWER MERCER	**22**		**2**						**24**
QUAKERTOWN	2								2
QUAKERTOWN NO 2			7						7
QUAKERTOWN	**2**		**7**						**9**
BROAS						14			14
BROAS, UPPER RIDER						1			1
HAZARD NO 9						4			4
HINDMAN						15			15
PR NCESS NO 4						2			2
STOCKTON					17				17
STOCKTON RIDER					1				1
STOCKTON-LEWISTON					1				1
T PTOP						4			4
UPPER BROAS						3			3
STOCKTON					**19**	**43**			**62**

COAL BED NAMES (COALQUAL database)	Number of Samples								
COAL BED NAMES (BOLD, THIS REPORT)	PA	MD	OH	nWV	sWV	KY	TN	VA	Total
COALBURG					22				22
COALBURG A					1				1
FRANCIS						9			9
FRANCIS R DER						4			4
HAZARD NO 7						19			19
HAZARD NO 8						9			9
HIGH SPLINT						1		1	2
LENOX						1			1
LOWER PEACH ORCHARD						9			9
M DDLE PEACH ORCHARD						1			1
MUDSEAM						6			6
PEACH ORCHARD						33			33
PEACH ORCHARD RIDER						1			1
PR NCESS NO 3						6			6
PR NCESS NO 3 RIDER						1			1
SEBASTIAN						3			3
UPPER PEACH ORCHARD						16			16
COALBURG					**23**	**119**		**1**	**143**
HAZARD						38			38
HAZARD NO 5A						2			2
HAZARD RIDER						5			5
INDEX						1			1
MORRIS						3		3	6
PEWEE							5		5
PRATER						3			3
RED SPR NGS						1			1
WIN FREDE					17	1			18
WINIFREDE/HAZARD					**17**	**54**	**5**	**3**	**79**
LOWER WINIFREDE/HAZARD						**10**			**10**
CHILTON A					1				1
COPLAND						3			3
LIMESTONE						1			1
PARDEE								5	5
TAYLOR						5			5
CHILTON/TAYLOR					**1**	**9**		**5**	**15**
BIG MARY						2	7		9
F RE CLAY RIDER						20			20
FIRE CLAY RIDER						**22**	**7**		**29**
CHILTON					2				2
F RE CLAY						40			40
HERNSHAW					2				2
HIGNITE						2			2
LITTLE FIRE CLAY						6			6
PH LL PS								1	1
STRAY						6			6
UPPER WHITESBURG						2			2
WALLINS CREEK						1			1
WALNUT MOUNTA N							2		2
WHITESBURG						2			2
WINDROCK							4		4
FIRE CLAY					**4**	**59**	**6**	**1**	**70**

Table 1. Coal bed names used in this report (names in bold), correlative alternate coal bed names used in COALQUAL database (see column CBED in Appendix 1), number of samples (N) from each state, and total number of samples for each coal bed (in bold) [nWV = northern West Virgina coal field sWV = southern West Virginia coal field]

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COAL BED NAMES (COALQUAL database)	Number of Samples								
COAL BED NAMES (BOLD, THIS REPORT)	**PA**	**MD**	**OH**	**nWV**	**sWV**	**KY**	**TN**	**VA**	**Total**
CEDAR GROVE					2				2
DINGESS					2				2
HERNSHAW					12				12
HOUSE								2	2
LOWER HIGNITE						2			2
LOWER WHITESBURG						3			3
UPPER WHITESBURG						3			3
WHITESBURG						11			11
WHITESBURG RIDER						2			2
CEDAR GROVE/WHITESBURG					**16**	**21**		**2**	**39**
ALMA					1				1
AMBURGY						7			7
CANNEL CITY						5			5
CREECH						3			3
GUN CREEK						1			1
JORDAN							1		1
LOW SPL NT						2	1	3	6
PEERLESS					1				1
PIONEER							1		1
POPLAR LICK						2	3		5
STERLING						1			1
WILLIAMSON						13			13
WILLIAMSON/AMBURGY					**2**	**34**	**6**	**3**	**45**
34 NCH								1	1
BUCKEYE SPRING						3			3
CAMPBELL CREEK					12				12
CEDAR GROVE					13				13
DARBY						3			3
KELLIOKA						4			4
LITTLE CANEY						7			7
LOWER CAMPBELL CREEK					4				4
LOWER CEDAR GROVE					6	2			8
NO 2 GAS					15				15
PEERLESS					12				12
TAGGART								9	9
TAGGART MARKER								3	3
TOM COOPER						1			1
UPPER CEDAR GROVE					7				7
UPPER ELKHORN 3 2ND RIDER						1			1
UPPER ELKHORN NO 3						29			29
UPPER ELKHORN NO 3 RIDER						1			1
UPPER ELKHORN NO 3 5						1			1
VAN LEAR						9			9
CAMPBELL CREEK/UPPER ELKHORN NO 3					**69**	**61**		**13**	**143**

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| COAL BED NAMES (COALQUAL database) | | | | | Number of Samples | | | | |
COAL BED NAMES (BOLD, THIS REPORT)	PA	MD	OH	nWV	sWV	KY	TN	VA	Total
ALMA					12	4			16
GRASSY						7			7
HARLAN						6			6
HUCKLEBERRY						4			4
JELLICO						26	3		29
JOYNER							1		1
M NGO						1			1
POWELLTON					10				10
POWELLTON A					1				1
RIM						2			2
UPPER ALMA						2			2
UPPER ELKHORN NO 1						8			8
UPPER ELKHORN NO 2						18			18
UPPER ELKHORN NO 2-1						2			2
UPPER ELKHORN NO 2-1 RIDER						1			1
UPPER ST CHARLES								1	1
WILSON								5	5
UPPER ELKHORN NOS. 1 AND 2/POWELLTON					23	81	4	6	114
KELLY								3	3
BLUE GEM						23	3		26
BLUE GEM RIDER						1			1
CAMPBELL CREEK					9			2	11
EAGLE					31				31
IMBODEN						1		9	10
IMBODEN MARKER								4	4
LITTLE BLUE GEM						1			1
LOWER CAMPBELL CREEK					1				1
LOWER ELKHORN						9			9
LOWER PATH FORK						1			1
NO 2 GAS					8				8
PATH FORK						3			3
POND CREEK						10			10
POND CREEK RIDER						2			2
STRAIGHT CREEK						2			2
V RES						1			1
POND CREEK					49	54	3	15	121
BLA R								17	17
BLA R MARKER								3	3
CLINTWOOD						3		55	58
CLINTWOOD MARKER								2	2
CLINTWOOD RIDER								1	1
COAL CREEK							3		3
COLONY						2			2
COLONY RIDER						1			1
HANCE						4			4
HANCE SPLIT 1						1			1
HANCE SPLIT 2						1			1
HANCE SPLIT 3						1			1
HANCE SPLIT 4						1			1
LILY						9			9
MANCHESTER						15			15
MATEWAN					2				2
RIVER GEM						1			1
RIVER GEM R DER						1			1
ZACHARIAH						3			3
MATEWAN/CLINTWOOD					2	43	3	78	126

COAL BED NAMES (COALQUAL database)					Number of Samples				
COAL BED NAMES (BOLD, THIS REPORT)	PA	MD	OH	nWV	sWV	KY	TN	VA	Total
EAGLE					5			1	6
LYONS								15	15
M LLARD						2			2
MIDDLE WAR EAGLE/EAGLE					**5**	**2**		**16**	**23**
BENS CREEK					5				5
GLAMORGAN						2			2
MASON						4	4		8
BENS CREEK/BLAIR					**5**	**6**	**4**		**15**
DORCHESTER								50	50
GLEN MARY							3		3
LITTLE EAGLE					3				3
LYONS								14	14
NORTON								16	16
POPLAR CREEK							1		1
POWELLTON					1				1
LITTLE EAGLE/DORCHESTER					**4**		**4**	**80**	**88**
GILBERT					2				2
HAGY						2		8	10
LOWER WAR EAGLE					1				1
LOWER WAR EAGLE/HAGY					**3**	**2**		**8**	**13**
GLENALUM TUNNEL					1				1
GRAY HAWK						7			7
REX							4		4
SPLASH DAM						1			1
SPLASHDAM								19	19
SPLITSEAM						3			3
GLENALUM TUNNEL/SPLASHDAM					**1**	**11**	**4**	**19**	**35**
BARREN FORK						5			5
BARREN FORK R DER						1			1
BEATTYVILLE						3			3
CORLEY HOLLOW						1			1
HALSEY ROUGH						3			3
LEE								5	5
UPPER BANNER								28	28
GILBERT A/UPPER BANNER						**13**		**33**	**46**
GILBERT					3				3
LOWER BANNER								20	20
GILBERT/LOWER BANNER					**3**			**20**	**23**
BIG FORK								**3**	**3**
DOUGLAS					4				4
KENNEDY								28	28
LOWER DOUGLAS					1				1
RED ASH RIDER								2	2
WIDOW KENNEDY								2	2
DOUGLAS/KENNEDY					**5**			**32**	**37**
JEWELL								11	11
RAVEN								6	6
RAVEN NO 1								3	3
STEARNS NO 2						4			4
JEWELL/RAVEN						**4**		**20**	**24**

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COAL BED NAMES (COALQUAL database)	Number of Samples								
COAL BED NAMES (BOLD, THIS REPORT)	PA	MD	OH	nWV	sWV	KY	TN	VA	Total
BEAVER CREEK						1			1
IAEGER					2				2
JAWBONE								22	22
JAWBONE RIDER								3	3
JAWBONE-T LLER								5	5
STEARNS NO 1 5						1			1
IAEGER/JAWBONE					**2**	**2**		**30**	**34**
STEARNS						8			8
STEARNS ZONE						1			1
T LLER								8	8
LOWER IAEGER/TILLER						**9**		**8**	**17**
CASTLE								4	4
CASTLE RIDER								1	1
SEWELL B					1				1
SEWELL B/GREASY CREEK					**1**			**5**	**6**
M DDLE SEABOARD								1	1
SEWELL A					5			1	6
SEWELL A					**5**			**2**	**7**
DIRTY NO 6								1	1
DIRTY SIX					1			1	2
DIRTY SIX					**1**			**2**	**3**
LOWER SEABOARD								8	8
SEWELL				1	39			4	44
SEWELL RIDER					3				3
SHARON NO 1			6						6
SEWELL/LOWER SEABOARD			**6**	**1**	**42**			**12**	**61**
SMITH						3		2	5
UPPER HORSEPEN								7	7
WELCH					1			2	3
WELCH/UPPER HORSEPEN					**1**	**3**		**11**	**15**
LITTLE RALEIGH/MIDDLE HORSEPEN					**7**			**1**	**8**
BECKLEY					25			2	27
BECKLEY RIDER					1				1
WAR CREEK								2	2
BECKLEY/WAR CREEK					**26**			**4**	**30**
F RE CREEK					19				19
F RE CREEK R DER								2	2
LOWER HORSEPEN								1	1
FIRE CREEK/LOWER HORSEPEN					**19**			**3**	**22**
POCAHONTAS NO. 10/LITTLE FIRE CREEK								**3**	**3**
COVE CREEK								7	7
POCAHONTAS NO 7					1				1
POCAHONTAS NO 7					**1**			**7**	**8**
POCAHONTAS NO 6					**13**				**13**
POCAHONTAS NO 4					**12**			**1**	**13**
POCAHONTAS NO 3					37			14	51
POCAHONTAS NO 3 RDR					2				2
POCAHONTAS NO 3					**39**			**14**	**53**
POCAHONTAS NO 1								**3**	**3**
Grand Total	**723**	**46**	**639**	**114**	**469**	**723**	**46**	**467**	**3227**

Table 1. Coal bed names used in this report (names in bold), correlative alternate coal bed names used in COALQUAL database (see column CBED in Appendix 1), number of samples (N) from each state, and total number of samples for each coal bed (in bold) [nWV = northern West Virgina coal field sWV = southern West Virginia coal field]

Table 2. Stratigraphic list of coal bed names used in this report and number (N) of samples, thick samples (≥28 inch), and thin samples (<28 inch).

Stratigraphic system, series, stage, and formation names have been debated and revised in the literature numerous times. We cite recent references for the stratigraphic intervals used in this table and report. * = some and ** = significant mountaintop mining, target coal beds. Coal bed code letters indicate coal beds with N ≥30 samples. SGB (selenium greater than background) indicates the stratigrahic interval with coal beds' average selenium concentration greater than average selenium concentration in Appalachian basin coal. Stratigraphic intervals pre-SGB, SGB, and post-SGB, this report, used in fig. 7 and table 5.

Table 2. Stratigraphic list of coal bed names used in this report and number (N) of samples, thick samples (≥28 inch), and thin samples (<28 inch).

System	Peppers (1996) western European — Series and Stage	Peppers (1996) Midcontinent — System	Peppers (1996) Midcontinent — Series	Peppers (1996), Blake (1998) West Virginia — Formation	Chesnut (1996) eastern Kentucky — Group and Formation	This report central and northern Appalachian basin — Coal bed names	All samples N	All samples coal bed code, N ≥30	Thick samples ≥28 inch N	Thick samples ≥28 inch coal bed code, N ≥30	Thin samples <28 inch N	Thin samples <28 inch coal bed code, N ≥30	This report Se trend — Interval
	Stephanian C	Upper Pennsylvaian	Virgilian	Monongahela	Monongahela	Waynesburg	60	A	56	A	4		post-SGB
						Sewickley	42	B	40	B	2		
						Fishpot	4		1		3		
						Redstone	74	C	56	C	18		
						Pittsburgh Roof	10		2		8		
						Pittsburgh	137	D	132	D	5		
	Stephanian B		Missourian	Conemaugh	Conemaugh	Elk Lick	3		2		1		
						Federal Hill	3		1		2		
	Stephanian A					Harlem	9		1		8		
						Upper Bakerstown	4		2		2		
						Lower Bakerstown	30	E	12		18		
						Wilgus	4		1		3		
						Brush Creek	11		3		8		
						Mahoning	20		6		14		
	Westphalian D		Desmoinsian	Allegheny/Charleston	Breathitt / Princess	Upper Freeport Rider	6		3		3		
						Upper Freeport	278	F	215	F	63	F	
						Lower Freeport	103	G	67	G	36	G	
						Upper Kittanning Rider	3				3		
						Upper Kittanning	67	H	32	H	35	H	
						Middle Kittanning Rider	8				8		
						Middle Kittanning	243	I	168	I	75	I	
						Strasburg	11		1		10		
						Lower Kittanning Rider	7		1		6		
						Lower Kittanning / ** No 6 block	198	J	141	J	57	J	
		sylvanian				Clarion	74	K	47	K	27		
						Brookville	73	L	30	L	43	L	
						** No 5 Block	93	M	65	M	28		
						* Stockton A / Little No 5 Block	4		2		2		
						Tionesta	5		4		1		
						Upper Mercer	8		2		6		

System	Stage	Series	Age	Division	Member	Seam	Total						SGB
Pennsylvanian	Westphalian C	Middle Penns	Atokan	Kanawha upper division	Breathitt / Four Corners	Lower Mercer	24		7		17		SGB
						Quakertown	9		2		7		
						** Stockton	62	N	51	N	11		
						** Coalburg	143	O	67	O	76	O	
						* Winifrede / Hazard	79	P	48	P	31	P	
						* Lower Winifrede / Hazard	10		4		6		
	Westphalian B			Kanawha middle division	Breathitt / Hyden	Chilton/Taylor	15		9		6		
						Fire Clay Rider	29		13		16		
						* Fire Clay	70	Q	40	Q	30	Q	
						* Cedar Grove / * Whitesburg	39	R	16		23		
					Breathitt / Pikeville	* Williamson / * Amburgy	45	S	19		26		pre-SGB
						* Campbell Creek / * Upper Elkhorn No 3	143	T	80	T	63	T	
						Upper Elkhorn Nos 1 and 2 / Powellton	114	U	59	U	55	U	
						Kelly	3		3				
						Pond Creek	121	V	78	V	43	V	
	Westphalian A	Lower Pennsylvanian	Morrowan	Kanawha lower division	Breathitt / Grundy	Matewan / Clintwood	126	W	54	W	72	W	
						Middle War Eagle / Eagle	23		12		11		
						Bens Creek / Blair	15		11		4		
						Little Eagle / Dorchester	88	X	54	X	34	X	
						Lower War Eagle / Hagy	13		8		5		
						Glenalum Tunnel / Splashdam	35	Y	17		18		
						Gilbert A / Upper Banner	46	Z	24		22		
						Gilbert / Lower Banner	23		17		6		
						Big Fork	3		2		1		
						Douglas / Kennedy	37	AA	22		15		
				New River	Breathitt / Alvy Creek	Jewell / Raven	24		19		5		
						Iaeger / Jawbone	34	BB	17		17		
						Lower Iaeger / Tiller	17		7		10		
					Breathitt / Bottom Creek	Sewell B / Greasy Creek	6		2		4		
						Sewell A	7		3		4		
						Dirty Six	3		3				
						Sewell / Lower Seaboard	61	CC	41	CC	20		
						Welch / Upper Horsepen	15		10		5		
						Little Raleigh / Middle Horsepen	8		5		3		
	Namurian C					Beckley / War Creek	30	DD	18		12		
						Fire Creek / Lower Horsepen	22		14		8		
						Pocahontas No 10 / Little Fire Creek	3		1		2		
	Namurian B			Pocahontas	Breathitt / Pocahontas	Pocahontas No 7	8		3		5		
						Pocahontas No 6	13		10		3		
						Pocahontas No 4	13		13				
						Pocahontas No 3	53	EE	43	EE	10		
						Pocahontas No 1	3				3		
						Grand Total	**3227**	**31**	**2019**	**23**	**1208**	**14**	

Table 3. Coal quality statistics by state for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese. [N = number of samples; nWV = northern West Virginia coal field; sWV = southern West Virginia coal field.]

Parameter	State	N	Average	Standard Deviation	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
			ppm	ppm	ppm	ppm	ppm	ppm	ppm
Selenium	PA	723	3.6	2.6	0.41	1.9	2.8	4.2	21
Selenium	MD	46	3.4	2.8	0.63	1.7	2.3	4.2	14
Selenium	OH	638	3.7	2.4	0.60	2.1	3.1	4.7	17
Selenium	nWV	113	2.5	2.3	0.20	1.1	1.7	2.7	14
Selenium	sWV	469	3.8	2.3	0.76	2.1	3.5	4.6	16
Selenium	KY	723	4.2	2.3	0.07	2.6	3.8	5.5	18
Selenium	TN	46	3.1	1.6	0.50	1.9	2.9	4.1	8
Selenium	VA	465	2.7	1.4	0.07	1.7	2.5	3.4	8
			in	in	in	in	in	in	in
Thickness	PA	723	36	19	2	23	33	47	115
Thickness	MD	46	34	23	8	20	27	40	112
Thickness	OH	639	37	15	9	27	36	45	125
Thickness	nWV	114	57	21	8	42	58	72	108
Thickness	sWV	469	39	19	4	27	38	49	172
Thickness	KY	723	29	18	3	16	26	39	156
Thickness	TN	46	34	13	9	26	33	40	84
Thickness	VA	467	33	16	5	22	31	41	128
			percent	percent	percent	percent	percent	percent	percent
Ash y\ield	PA	665	12.87	5.24	1.70	8.98	11.82	15.90	31.20
Ash y\ield	MD	45	14.56	6.64	5.55	9.78	13.01	18.40	29.31
Ash y\ield	OH	625	11.94	5.20	2.20	8.60	10.91	14.32	32.40
Ash y\ield	nWV	94	9.95	3.64	5.60	7.23	9.05	11.40	20.90
Ash y\ield	sWV	449	8.68	5.13	0.90	5.10	7.40	10.70	31.50
Ash y\ield	KY	695	9.59	5.47	0.90	5.51	8.57	12.66	32.90
Ash y\ield	TN	46	7.48	5.59	1.60	3.20	5.10	10.80	22.00
Ash y\ield	VA	433	8.30	5.28	1.66	4.50	6.60	10.51	30.90
			percent	percent	percent	percent	percent	percent	percent
Sulfur	PA	717	2.48	1.45	0.39	1.44	2.20	3.21	9.34
Sulfur	MD	45	2.16	1.39	0.40	1.17	1.99	2.80	8.00
Sulfur	OH	625	3.53	1.53	0.50	2.50	3.40	4.50	10.60
Sulfur	nWV	95	2.55	1.16	0.40	1.75	2.60	3.20	6.80
Sulfur	sWV	449	0.97	0.62	0.40	0.60	0.80	1.10	6.30
Sulfur	KY	695	1.65	1.29	0.40	0.71	1.08	2.20	8.90
Sulfur	TN	46	1.71	1.31	0.50	0.80	1.20	2.18	5.20
Sulfur	VA	433	1.19	0.89	0.40	0.68	0.85	1.27	6.61

Table 3. Coal quality statistics by state for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese. [N = number of samples; nWV = northern West Virginia coal field; sWV = southern West Virginia coal field.]

Parameter	State	N	Average	Standard Deviation	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
			percent	percent	percent	percent	percent	percent	percent
Pyritic sulfur	PA	688	1.61	1.25	0.01	0.71	1.38	2.17	7.31
Pyritic sulfur	MD	45	1.41	1.20	0.01	0.57	1.22	1.94	6.18
Pyritic sulfur	OH	625	2.10	1.24	0.03	1.22	1.90	2.78	8.97
Pyritic sulfur	nWV	22	1.31	0.85	0.13	0.74	1.22	1.69	3.18
Pyritic sulfur	sWV	84	0.30	0.41	0.02	0.07	0.17	0.32	2.14
Pyritic sulfur	KY	694	0.89	1.11	0.01	0.11	0.35	1.30	7.62
Pyritic sulfur	TN	46	0.79	0.98	0.03	0.10	0.39	1.01	3.65
Pyritic sulfur	VA	427	0.49	0.70	0.01	0.09	0.21	0.52	5.22
			ppm	ppm	ppm	ppm	ppm	ppm	ppm
Arsenic	PA	719	34	39	0.31	11.0	22	43	410
Arsenic	MD	46	25	21	0.80	9.9	18	31	79
Arsenic	OH	638	24	33	0.49	5.8	13	31	390
Arsenic	nWV	113	19	21	0.90	6.9	11	20	100
Arsenic	sWV	467	11	16	0.08	1.8	5	12	130
Arsenic	KY	718	29	52	0.50	3.8	11	34	680
Arsenic	TN	46	24	32	0.30	3.1	10	34	160
Arsenic	VA	466	20	31	0.45	3.4	8	21	330
			ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mercury	PA	723	0.28	0.26	0.003	0.110	0.22	0.38	2.9
Mercury	MD	46	0.33	0.40	0.003	0.085	0.18	0.32	1.6
Mercury	OH	639	0.21	0.15	0.003	0.100	0.17	0.27	1.1
Mercury	nWV	114	0.25	0.20	0.007	0.120	0.20	0.30	1.0
Mercury	sWV	469	0.13	0.16	0.007	0.043	0.08	0.16	1.8
Mercury	KY	721	0.18	0.17	0.007	0.060	0.13	0.24	1.5
Mercury	TN	46	0.16	0.15	0.007	0.038	0.12	0.22	0.6
Mercury	VA	466	0.11	0.11	0.003	0.045	0.07	0.16	0.8
			ppm	ppm	ppm	ppm	ppm	ppm	ppm
Manganese	PA	720	25	40	0.9	8.5	15	25	470
Manganese	MD	46	18	18	1.1	6.7	12	22	90
Manganese	OH	639	31	47	2.5	13.0	20	33	690
Manganese	nWV	114	28	34	2.8	12.0	21	29	290
Manganese	sWV	468	20	44	0.7	4.3	8	17	540
Manganese	KY	721	18	43	1.2	5.4	9	17	660
Manganese	TN	46	15	14	2.8	5.7	11	18	70
Manganese	VA	466	21	27	0.8	6.2	12	23	260

Table 4. Coal quality statistics for coal beds with≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4a. Coal Samples, all thicknesses.

				Selenium							
Coal bed name, this repor	Thickness range	Coal bed code N ≥ 30	N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quartile ppm	Maximum ppm
Waynesburg	all	A	60	2.6	2.8	0.90	0.64	2.4	2.9	3.3	5.5
Sewickley	all	B	42	2.6	2.9	1.3	0.70	2.1	2.6	3.7	7.2
Redstone	all	C	74	2.0	2.2	1.2	0.50	1.4	2.0	2.6	7.0
Pittsburgh Roof	all		10	1.9	2.1	1.1	0.60	1.5	1.8	2.6	4.4
Pittsburgh	all	D	137	1.4	1.7	1.2	0.20	1.0	1.4	2.0	7.5
Harlem	all		9	1.1	1.2	0.32	0.68	0.90	1.2	1.4	1.6
Lower Bakerstown	all	E	30	3.1	3.5	1.9	1.5	2.4	3.3	4.2	11
Brush Creek	all		11	2.7	3.0	1.6	1.2	2.0	2.9	3.5	6.4
Mahoning	all		20	2.0	2.2	1.1	1.2	1.5	1.9	2.5	4.7
Upper Freeport Rider	all		6	2.8	3.2	1.5	1.4	1.8	3.5	4.2	5.1
Upper Freeport	all	F	277	2.4	2.8	2.0	0.43	1.7	2.2	3.1	14
Lower Freeport	all	G	102	3.3	3.9	2.6	0.90	2.2	3.3	4.7	15
Upper Kittanning	all	H	67	3.8	4.6	2.9	1.3	2.3	3.4	6.0	13
Middle Kittanning Rider	all		8	4.5	5.2	2.3	1.0	3.6	5.9	6.6	8.1
Middle Kittanning	all	I	243	3.2	3.6	2.1	1.0	2.4	3.1	4.2	17
Strasburg	all		11	3.6	3.9	1.6	1.5	3.6	3.9	4.1	7.7
Lower Kittanning Rider	all		7	3.4	3.9	2.5	1.6	2.4	3.1	4.4	8.9
Lower Kittanning/No 6 block	all	J	198	3.4	4.0	2.6	0.60	2.2	3.5	5.1	20
Clarion	all	K	74	5.6	6.2	2.5	1.2	4.7	6.1	7.6	14
Brookville	all	L	73	4.9	5.7	3.4	1.2	3.5	4.8	7.4	21
No 5 Block	all	M	93	6.2	7.1	3.1	0.10	5.2	6.9	8.9	18
Tionesta	all		5	7.7	8.1	2.9	5.8	6.2	7.1	8.2	13
Upper Mercer	all		8	7.7	8.6	4.3	3.1	5.8	7.2	12	16
Lower Mercer	all		24	6.2	7.1	3.1	0.84	5.6	6.6	8.8	13
Quakertown	all		9	5.9	7.2	4.2	1.2	4.5	5.7	12	12
Stockton	all	N	62	5.2	5.6	1.9	2.4	4.1	5.2	7.1	11
Coalburg	all	O	143	4.7	5.0	1.9	1.2	3.8	4.9	6.1	12
Winifrede/Hazard	all	P	79	4.4	4.7	1.8	0.50	3.5	4.6	5.7	11
Lower Winifrede/Hazard	all		10	2.8	4.0	2.0	0.07	3.4	4.0	5.0	7.4
Chilton/Taylor	all		15	3.1	3.7	2.2	0.73	2.4	3.4	4.4	8.7
Fire Clay Rider	all		29	4.0	4.5	2.6	1.7	3.2	4.1	4.9	13
Fire Clay	all	Q	70	3.6	3.9	1.6	1.3	2.7	3.5	5.0	9.0
Cedar Grove/Whitesburg	all	R	39	3.8	4.1	1.8	1.2	2.8	3.8	4.7	9.4
Williamson/Amburgy	all	S	45	3.0	3.3	1.6	0.90	2.1	3.0	4.2	7.5
Campbell Creek/Upper Elkhorn No 3	all	T	143	3.4	3.8	1.6	0.07	2.7	3.6	4.6	9.3
Upper Elkhorn Nos 1 and 2/Powellton	all	U	114	3.0	3.5	2.0	0.64	2.2	3.2	4.1	16
Pond Creek	all	V	121	3.2	3.4	1.2	1.2	2.5	3.2	4.2	6.7
Matewan/Clintwood	all	W	126	2.4	2.8	1.6	0.54	1.7	2.5	3.4	8.0
Middle War Eagle/Eagle	all		23	3.1	3.5	2.1	1.1	2.2	3.1	4.3	9.3
Bens Creek/Blair	all		15	2.0	2.2	0.88	0.80	1.8	2.0	2.5	4.2
Little Eagle/Dorchester	all	X	87	2.3	2.7	1.6	0.63	1.7	2.2	3.3	7.1
Lower War Eagle/Hagy	all		13	2.9	3.1	0.76	1.3	2.7	3.2	3.6	4.0
Glenalum Tunnel/Splashdam	all	Y	35	2.4	2.5	0.82	0.76	1.9	2.5	3.0	4.4
Gilbert A/Upper Banner	all	Z	46	2.7	3.0	1.3	1.2	2.2	2.7	3.5	6.7
Gilbert/Lower Banner	all		23	2.7	2.9	1.1	1.4	2.3	2.7	3.1	6.3
Douglas/Kennedy	all	AA	37	1.8	2.2	1.8	0.40	1.2	1.6	2.6	11
Jewell/Raven	all		24	1.9	2.2	1.2	0.20	1.5	2.1	2.7	5.9
Iaeger/Jawbone	all	BB	34	2.1	2.7	1.9	0.07	1.7	2.5	3.2	11
Lower Iaeger/Tiller	all		17	2.5	2.7	1.0	1.0	2.1	2.7	2.9	5.4
Sewell B/Greasy Creek	all		6	2.0	2.3	1.3	1.2	1.3	1.7	3.4	4.0
Sewell A	all		7	1.8	1.9	0.64	0.93	1.5	1.6	2.5	2.6
Sewell/Lower Seaboard	all	CC	61	2.0	2.6	2.2	0.76	1.3	1.8	2.8	14
Welch/Upper Horsepen	all		15	1.6	1.8	0.79	0.70	1.2	1.8	2.2	3.6
Little Raleigh/Middle Horsepen	all		8	2.1	2.2	0.63	1.1	1.9	2.1	2.6	3.1
Beckley/War Creek	all	DD	30	1.6	1.8	1.2	0.78	1.3	1.5	2.0	7.0
Fire Creek/Lower Horsepen	all		22	2.1	2.4	1.2	0.67	1.6	2.1	3.1	4.9
Pocahontas No 7	all		7	1.6	1.8	1.0	1.0	1.2	1.4	1.8	4.0
Pocahontas No 6	all		13	2.5	2.8	1.3	1.1	2.0	2.3	3.3	5.9
Pocahontas No 4	all		13	2.4	2.5	1.1	1.8	2.0	2.3	2.5	5.9
Pocahontas No 3	all	EE	53	3.1	3.4	1.7	1.1	2.3	2.9	4.1	8.2

Table 4. Coal quality statistics for coal beds with≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4a. Coal Samples, all thicknesses.

Coal Bed Name This Study	Thickness range	Coal bed code N ≥ 30	N	Geometric mean in	Average in	Standard Deviation in	Minimum in	Lower Quartile in	Median in	Upper Quartile in	Maximum in
Waynesburg	all	A	60	45.3	48.1	17.3	20.5	35.9	43.2	57.8	95.0
Sewickley	all	B	42	44.7	46.3	12.3	19.8	38.5	46.5	54.8	87.5
Redstone	all	C	74	40.4	45.5	20.3	12.0	28.1	47.3	61.8	88.0
Pittsburgh Roof	all		10	22.7	24.2	8.6	10.2	20.1	23.5	27.3	42.0
Pittsburgh	all	D	137	57.7	61.8	21.8	9.0	47.0	59.5	75.5	125.0
Harlem	all		9	23.9	24.3	4.7	17.5	20.0	25.8	27.0	32.0
Lower Bakerstown	all	E	30	27.4	28.7	8.9	13.2	23.3	27.0	32.9	56.0
Brush Creek	all		11	18.4	20.8	10.4	7.8	14.4	20.0	26.7	38.0
Mahoning	all		20	22.0	24.7	12.2	4.8	17.6	22.0	29.3	63.0
Upper Freeport Rider	all		6	24.0	25.4	8.7	15.0	18.0	27.5	30.6	36.0
Upper Freeport	all	F	278	36.7	41.3	18.0	2.0	29.3	42.0	49.2	105.5
Lower Freeport	all	G	103	31.0	34.8	16.0	5.4	25.1	32.6	42.5	74.0
Upper Kittanning	all	H	67	26.9	30.7	16.5	6.6	19.8	26.4	37.2	94.8
Middle Kittanning Rider	all		8	12.6	15.2	8.3	3.0	11.4	15.0	19.5	27.6
Middle Kittanning	all	I	243	31.3	34.1	13.2	2.5	26.0	34.0	41.4	95.5
Strasburg	all		11	18.8	19.8	6.8	12.8	14.3	17.5	23.9	33.0
Lower Kittanning Rider	all		7	13.7	17.3	15.6	6.6	9.9	12.0	15.6	51.6
Lower Kittanning/No 6 block	all	J	198	32.2	34.1	11.7	9.8	26.4	33.3	39.2	86.4
Clarion	all	K	74	29.6	33.7	17.2	9.0	20.1	31.6	42.6	96.0
Brookville	all	L	73	24.3	27.4	13.6	6.6	17.0	23.0	36.0	61.5
No 5 Block	all	M	93	37.7	47.0	32.5	7.4	24.0	40.0	55.0	171.8
Tionesta	all		5	31.9	36.0	15.1	10.5	36.6	39.5	44.3	49.3
Upper Mercer	all		8	21.7	23.8	10.8	11.4	15.9	21.9	29.3	40.5
Lower Mercer	all		24	24.6	26.8	12.2	10.8	21.9	24.3	30.2	69.6
Quakertown	all		9	24.1	24.7	6.1	18.5	19.8	24.0	26.0	38.4
Stockton	all	N	62	37.0	43.0	19.6	5.9	30.2	45.5	54.1	93.3
Coalburg	all	O	143	26.6	32.5	20.8	4.3	17.6	26.8	45.0	112.5
Winifrede/Hazard	all	P	79	27.6	31.9	15.8	4.3	20.3	31.0	40.0	73.2
Lower Winifrede/Hazard	all		10	20.7	22.7	8.9	6.7	17.7	24.2	29.1	35.8
Chilton/Taylor	all		15	24.5	32.1	22.1	5.5	14.4	31.1	41.4	85.2
Fire Clay Rider	all		29	21.6	27.9	19.5	6.0	10.2	27.2	38.0	91.3
Fire Clay	all	Q	70	28.5	33.4	17.5	6.0	20.0	32.0	44.0	80.5
Cedar Grove/Whitesburg	all	R	39	21.6	25.9	13.6	3.1	15.3	23.5	34.7	52.0
Williamson/Amburgy	all	S	45	23.0	27.4	16.5	5.5	14.6	24.0	38.9	84.0
Campbell Creek/Upper Elkhorn No 3	all	T	143	27.5	30.6	13.8	7.0	20.8	29.7	38.2	85.5
Upper Elkhorn Nos 1 and 2/Powellton	all	U	114	24.7	28.5	14.2	7.1	16.0	28.3	39.0	69.3
Pond Creek	all	V	121	30.8	35.2	16.5	4.0	23.6	34.0	44.1	85.4
Matewan/Clintwood	all	W	126	23.6	26.4	12.7	7.7	17.7	25.0	33.5	87.2
Middle War Eagle/Eagle	all		23	27.5	30.0	13.0	12.6	20.1	28.8	37.8	64.8
Bens Creek/Blair	all		15	27.4	30.2	11.6	7.0	25.3	31.0	35.7	50.0
Little Eagle/Dorchester	all	X	88	28.9	31.2	11.8	10.2	22.0	32.4	37.2	66.0
Lower War Eagle/Hagy	all		13	26.0	28.2	9.0	6.0	22.8	28.8	33.6	39.0
Glenalum Tunnel/Splashdam	all	Y	35	27.4	30.7	14.7	11.0	17.3	27.6	40.8	69.0
Gilbert A/Upper Banner	all	Z	46	25.5	30.0	18.1	6.3	17.4	29.4	37.1	110.2
Gilbert/Lower Banner	all		23	36.6	40.1	16.0	12.8	29.3	41.0	45.7	71.0
Douglas/Kennedy	all	AA	37	30.9	32.2	9.7	18.0	26.5	30.5	36.0	62.0
Jewell/Raven	all		24	30.9	35.6	15.6	6.0	29.5	37.0	43.3	68.4
Iaeger/Jawbone	all	BB	34	29.1	33.4	17.2	8.4	24.6	28.6	41.0	77.8
Lower Iaeger/Tiller	all		17	18.4	23.9	17.7	5.4	9.0	18.0	35.9	68.4
Sewell B/Greasy Creek	all		6	21.4	23.2	10.2	13.0	16.7	18.8	32.0	36.0
Sewell A	all		7	26.7	28.8	11.3	12.0	23.3	27.8	34.5	46.0
Sewell/Lower Seaboard	all	CC	61	33.0	35.9	14.6	12.5	24.0	35.9	44.0	70.6
Welch/Upper Horsepen	all		15	33.1	40.5	30.3	11.0	24.0	31.0	43.0	128.0
Little Raleigh/Middle Horsepen	all		8	32.2	34.8	13.0	17.0	22.5	42.0	42.0	51.0
Beckley/War Creek	all	DD	30	28.8	33.2	17.6	8.0	23.3	29.0	40.1	87.0
Fire Creek/Lower Horsepen	all		22	31.5	34.7	15.9	14.0	21.3	31.9	40.5	70.0
Pocahontas No 7	all		8	21.8	24.2	11.7	10.5	16.3	20.1	34.8	42.5
Pocahontas No 6	all		13	32.5	33.2	6.6	23.0	30.1	33.3	38.0	43.5
Pocahontas No 4	all		13	64.8	65.9	12.6	49.0	60.1	62.6	76.0	91.0
Pocahontas No 3	all	EE	53	41.7	45.9	18.3	11.1	34.0	47.4	55.8	94.0

Table 4. Coal quality statistics for coal beds with≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4a. Coal Samples, all thicknesses.

Coal Bed Name This Study	Thickness range	Coal bed code N ≥ 30	N	Ash Yield Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quartile percent	Maximum percent
Waynesburg	all	A	57	16.65	17.20	3.71	3.16	15.63	17.16	19.37	29.70
Sewickley	all	B	40	11.59	11.98	3.10	5.70	9.72	11.50	13.83	20.20
Redstone	all	C	71	10.20	10.96	4.69	5.60	7.80	9.80	12.00	27.20
Pittsburgh Roof	all		10	14.63	15.30	4.39	6.80	12.95	15.62	17.25	22.30
Pittsburgh	all	D	129	10.00	10.51	3.83	4.40	8.20	10.18	11.72	32.03
Harlem	all		9	9.83	10.05	2.23	7.30	7.79	9.80	11.60	13.02
Lower Bakerstown	all	E *	29	11.47	12.74	6.22	5.55	8.65	10.52	14.74	29.30
Brush Creek	all		11	11.80	12.49	4.92	7.17	9.90	11.28	13.92	25.50
Mahoning	all		17	11.09	11.59	3.83	7.00	9.02	10.27	13.05	20.23
Upper Freeport Rider	all		6	12.61	14.05	8.09	8.10	8.89	11.81	14.19	29.70
Upper Freeport	all	F	218	12.36	13.26	5.08	3.60	9.90	12.03	15.69	29.31
Lower Freeport	all	G	103	10.60	11.61	5.38	3.90	8.23	10.00	14.48	31.20
Upper Kittanning	all	H	65	12.43	13.14	4.48	4.54	10.71	12.21	15.05	30.21
Middle Kittanning Rider	all		8	9.03	10.13	5.68	4.50	7.50	8.80	10.65	22.70
Middle Kittanning	all	I	239	9.43	10.71	5.33	1.70	6.85	9.73	14.16	28.66
Strasburg	all		11	11.32	11.73	3.15	6.30	9.80	11.80	13.57	16.80
Lower Kittanning Rider	all		7	11.43	13.08	7.50	5.70	7.49	12.90	15.29	27.44
Lower Kittanning/No 6 block	all	J	193	10.69	11.64	5.01	2.80	8.02	10.82	13.70	31.50
Clarion	all	K	74	12.98	14.07	5.43	4.20	10.19	13.95	17.09	28.38
Brookville	all	L	72	12.12	13.19	5.60	5.30	8.86	12.55	16.30	29.45
No 5 Block	all	M	85	10.70	11.83	5.52	2.70	7.80	10.59	14.50	31.50
Tionesta	all		5	13.58	15.26	9.64	9.82	10.62	10.75	12.70	32.40
Upper Mercer	all		8	18.07	18.61	4.48	10.40	16.57	19.08	21.11	24.52
Lower Mercer	all		23	15.22	16.18	5.32	4.80	12.78	15.07	19.73	27.09
Quakertown	all		9	11.09	12.10	4.35	3.30	10.33	12.81	14.42	17.40
Stockton	all	N	60	11.48	12.64	5.61	4.22	8.53	12.39	14.72	29.60
Coalburg	all	O	142	9.55	10.87	5.56	2.70	6.91	10.04	13.33	30.70
Winifrede/Hazard	all	P	77	8.62	10.39	6.13	2.00	5.20	9.49	14.27	28.50
Lower Winifrede/Hazard	all		10	7.43	8.26	3.81	3.50	5.66	7.43	10.82	15.10
Chilton/Taylor	all		15	11.56	12.53	5.75	5.70	8.95	12.70	13.54	30.00
Fire Clay Rider	all		23	11.38	12.88	6.96	3.65	8.75	11.12	16.05	32.90
Fire Clay	all	Q	66	9.66	11.08	5.85	2.50	6.79	10.66	13.88	31.80
Cedar Grove/Whitesburg	all	R	37	9.25	10.26	4.58	2.47	7.60	9.80	12.20	23.30
Williamson/Amburgy	all	S	44	7.61	8.76	4.99	2.30	5.86	7.72	10.77	26.10
Campbell Creek/Upper Elkhorn No 3	all	T	142	6.25	7.30	3.87	0.90	4.35	6.86	9.40	21.60
Upper Elkhorn Nos 1 and 2/Powellton	all	U	111	5.88	6.81	3.91	1.60	4.33	6.04	8.35	22.37
Pond Creek	all	V	121	6.32	7.40	3.95	1.22	4.50	6.70	10.20	16.80
Matewan/Clintwood	all	W	125	5.99	6.78	3.54	1.73	4.10	6.00	8.70	21.60
Middle War Eagle/Eagle	all		21	5.16	5.88	3.17	1.66	3.79	5.50	6.70	14.01
Bens Creek/Blair	all		15	5.08	7.20	6.26	1.60	2.65	4.34	10.40	18.30
Little Eagle/Dorchester	all	X	88	6.57	8.01	5.31	1.93	4.38	5.77	10.97	28.20
Lower War Eagle/Hagy	all		12	9.63	10.70	5.16	4.30	8.14	9.99	12.30	22.80
Glenalum Tunnel/Splashdam	all	Y	35	6.01	7.70	5.87	1.74	3.65	6.10	9.35	25.30
Gilbert A/Upper Banner	all	Z	41	7.64	8.38	3.92	3.60	5.99	6.94	10.30	20.67
Gilbert/Lower Banner	all		20	9.08	10.20	4.87	3.40	6.46	10.12	12.83	19.63
Douglas/Kennedy	all	AA	32	6.29	7.67	6.07	2.75	4.41	5.82	8.15	29.55
Jewell/Raven	all		19	6.41	7.95	5.75	2.40	3.95	5.90	9.83	24.59
Iaeger/Jawbone	all	BB	33	9.33	12.03	8.06	2.00	6.50	10.50	16.10	30.90
Lower Iaeger/Tiller	all		17	8.48	9.64	4.84	2.90	6.10	8.81	12.20	19.40
Sewell B/Greasy Creek	all		5	10.02	10.88	5.12	5.90	7.46	10.31	11.64	19.09
Sewell A	all		5	5.66	6.80	5.38	3.70	3.90	4.20	5.90	16.30
Sewell/Lower Seaboard	all	CC	52	6.27	7.39	4.59	2.30	3.95	6.15	9.23	21.60
Welch/Upper Horsepen	all		9	6.83	7.42	3.09	3.40	5.20	8.00	8.30	13.19
Little Raleigh/Middle Horsepen	all		6	8.75	10.59	8.62	5.10	5.98	7.80	9.18	27.85
Beckley/War Creek	all	DD *	27	6.19	7.64	5.61	0.90	4.60	6.70	8.00	29.30
Fire Creek/Lower Horsepen	all		22	6.23	6.91	3.31	2.60	5.03	6.50	8.63	17.20
Pocahontas No 7	all		8	9.40	11.23	8.09	4.60	7.44	8.74	10.96	29.25
Pocahontas No 6	all		13	7.33	7.98	3.78	4.30	5.60	6.90	9.60	17.90
Pocahontas No 4	all		13	6.14	6.35	1.84	4.20	5.60	5.93	6.60	11.40
Pocahontas No 3	all	EE	49	7.68	8.61	4.45	2.90	5.80	7.30	10.60	26.00

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4a. Coal Samples, all thicknesses.

Coal Bed Name This Study	Thickness range	Coal bed code N ≥ 30	N	Sulfur							
				Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quartile percent	Maximum percent
Waynesburg	all	A	58	2.58	2.77	0.98	0.70	2.20	2.67	3.40	5.20
Sewickley	all	B	40	2.64	2.95	1.28	0.70	2.05	2.96	3.74	5.90
Redstone	all	C	71	2.64	2.84	1.05	0.80	2.18	2.70	3.24	5.90
Pittsburgh Roof	all		10	2.23	2.88	1.99	0.60	1.26	2.30	4.38	6.50
Pittsburgh	all	D	129	2.94	3.34	1.48	0.40	2.22	3.40	4.50	6.70
Harlem	all		9	1.38	1.70	1.12	0.50	0.80	1.26	2.70	3.66
Lower Bakerstown	all	E *	29	2.32	2.66	1.22	0.40	1.72	2.69	3.31	5.41
Brush Creek	all		11	2.46	3.01	1.88	0.39	2.05	2.39	3.36	7.50
Mahoning	all		17	2.08	2.41	1.27	0.63	1.43	1.93	3.22	5.10
Upper Freeport Rider	all		6	1.97	2.72	2.08	0.50	1.10	2.27	4.46	5.40
Upper Freeport	all	F	270	2.16	2.45	1.29	0.59	1.55	2.19	3.05	8.00
Lower Freeport	all	G	103	2.33	2.77	1.48	0.50	1.83	2.64	3.68	7.22
Upper Kittanning	all	H	65	1.73	2.11	1.25	0.40	1.00	1.96	3.02	5.72
Middle Kittanning Rider	all		8	1.25	1.79	1.47	0.50	0.50	1.55	2.63	4.40
Middle Kittanning	all	I	239	2.63	3.01	1.45	0.50	1.99	2.89	3.90	8.11
Strasburg	all		11	4.28	4.88	1.98	1.10	4.41	5.59	6.14	7.20
Lower Kittanning Rider	all		7	1.33	1.49	0.80	0.82	0.91	1.00	1.95	2.93
Lower Kittanning/No 6 block	all	J	193	2.93	3.47	1.81	0.40	2.22	3.30	4.66	10.40
Clarion	all	K	74	3.09	3.53	1.61	0.50	2.41	3.59	4.38	9.34
Brookville	all	L	72	2.65	3.08	1.81	0.70	1.98	2.60	3.65	10.40
No 5 Block	all	M	85	0.95	1.15	0.89	0.40	0.66	0.80	1.20	4.87
Tionesta	all		5	3.99	4.92	3.49	1.38	2.97	4.80	4.83	10.60
Upper Mercer	all		8	3.53	3.73	1.31	2.19	2.77	3.70	4.45	5.96
Lower Mercer	all		23	2.13	2.58	1.58	0.51	1.47	1.91	3.75	6.15
Quakertown	all		9	1.70	2.35	2.19	0.55	0.90	1.71	2.40	7.21
Stockton	all	N	60	1.02	1.33	1.19	0.50	0.60	0.77	1.43	5.50
Coalburg	all	O	142	1.04	1.24	0.88	0.40	0.70	0.90	1.37	4.70
Winifrede/Hazard	all	P	77	0.91	1.05	0.71	0.41	0.66	0.80	1.10	4.70
Lower Winifrede/Hazard	all		10	0.91	0.99	0.48	0.60	0.69	0.77	1.21	2.14
Chilton/Taylor	all		15	1.45	1.78	1.27	0.60	0.90	1.20	2.77	4.90
Fire Clay Rider	all		23	2.24	2.70	1.52	0.69	1.32	2.80	3.60	5.20
Fire Clay	all	Q	66	1.00	1.18	0.91	0.50	0.70	0.83	1.22	5.95
Cedar Grove/Whitesburg	all	R	37	1.39	1.73	1.22	0.60	0.83	1.20	2.42	4.53
Williamson/Amburgy	all	S	44	1.50	1.84	1.25	0.59	0.80	1.47	2.44	5.80
Campbell Creek/Upper Elkhorn No 3	all	T	142	1.12	1.35	0.95	0.46	0.70	0.90	1.80	5.10
Upper Elkhorn Nos 1 and 2/Powellton	all	U	111	1.25	1.59	1.28	0.50	0.74	1.00	1.95	6.60
Pond Creek	all	V	121	1.09	1.37	1.09	0.41	0.65	0.90	1.61	6.30
Matewan/Clintwood	all	W	125	1.28	1.62	1.28	0.50	0.76	1.08	2.10	6.61
Middle War Eagle/Eagle	all		21	1.33	1.58	0.89	0.46	0.90	1.40	2.40	3.10
Bens Creek/Blair	all		15	1.17	1.38	0.89	0.50	0.80	1.00	1.88	3.56
Little Eagle/Dorchester	all	X	88	1.10	1.24	0.79	0.50	0.82	1.00	1.31	5.00
Lower War Eagle/Hagy	all		12	1.56	1.80	0.99	0.60	1.13	1.41	2.61	3.60
Glenalum Tunnel/Splashdam	all	Y	35	1.01	1.29	1.16	0.60	0.65	0.72	1.24	5.20
Gilbert A/Upper Banner	all	Z	41	1.03	1.29	1.03	0.40	0.60	0.90	1.67	5.80
Gilbert/Lower Banner	all		20	0.92	1.01	0.50	0.56	0.60	0.80	1.13	2.19
Douglas/Kennedy	all	AA	32	0.94	1.05	0.58	0.50	0.70	0.80	1.31	2.93
Jewell/Raven	all		19	0.96	1.29	1.27	0.50	0.60	0.75	1.14	4.20
Iaeger/Jawbone	all	BB	33	0.84	1.12	1.15	0.50	0.60	0.60	0.80	4.90
Lower Iaeger/Tiller	all		17	1.67	2.77	2.63	0.50	0.60	1.59	4.20	8.90
Sewell B/Greasy Creek	all		5	1.36	1.52	0.75	0.60	1.13	1.39	1.96	2.54
Sewell A	all		5	0.65	0.66	0.13	0.50	0.60	0.60	0.80	0.80
Sewell/Lower Seaboard	all	CC	52	0.82	0.91	0.48	0.40	0.60	0.80	1.05	2.58
Welch/Upper Horsepen	all		9	0.81	0.86	0.32	0.50	0.72	0.80	1.00	1.40
Little Raleigh/Middle Horsepen	all		6	0.72	0.75	0.21	0.50	0.58	0.80	0.88	1.00
Beckley/War Creek	all	DD *	27	0.87	1.00	0.61	0.40	0.60	0.80	1.25	3.20
Fire Creek/Lower Horsepen	all		22	0.86	0.90	0.28	0.40	0.70	0.85	1.10	1.50
Pocahontas No 7	all		8	0.76	0.81	0.33	0.50	0.56	0.63	1.15	1.27
Pocahontas No 6	all		13	1.00	1.06	0.43	0.50	0.80	0.90	1.20	2.30
Pocahontas No 4	all		13	0.64	0.65	0.12	0.50	0.60	0.65	0.70	0.88
Pocahontas No 3	all	EE	49	0.69	0.74	0.33	0.40	0.50	0.60	0.80	1.80

Table 4. Coal quality statistics for coal beds with≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4a. Coal Samples, all thicknesses.

				Pyritic Sulfur							
Coal Bed Name This Study	Thickness range	Coal bed code N ≥ 30	N	Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quartile percent	Maximum percent
Waynesburg	all	A	50	1.49	1.83	0.95	0.05	1.11	1.77	2.33	4.00
Sewickley	all	B	38	1.09	1.45	0.78	0.02	0.96	1.35	1.94	2.87
Redstone	all	C	35	1.63	1.90	1.00	0.19	1.24	1.75	2.41	4.93
Pittsburgh Roof	all		10	1.01	1.99	1.84	0.03	0.55	1.31	3.23	5.74
Pittsburgh	all	D	99	1.66	2.09	1.07	0.05	1.39	2.02	2.89	5.16
Harlem	all		9	0.60	0.94	0.81	0.07	0.26	0.62	1.22	2.44
Lower Bakerstown	all	E *	29	1.12	1.61	0.90	0.01	0.74	1.69	2.25	3.46
Brush Creek	all		11	1.45	2.18	1.75	0.05	1.31	1.52	2.38	6.45
Mahoning	all		16	0.90	1.44	0.98	0.02	0.70	1.36	2.08	3.34
Upper Freeport Rider	all		6	0.50	1.90	1.95	0.01	0.26	1.42	3.57	4.39
Upper Freeport	all	F	264	1.22	1.58	1.10	0.05	0.81	1.35	1.89	6.18
Lower Freeport	all	G	102	1.15	1.77	1.15	0.01	0.95	1.64	2.50	5.43
Upper Kittanning	all	H	63	0.72	1.40	1.17	0.01	0.37	1.41	2.15	5.41
Middle Kittanning Rider	all		8	0.30	1.06	1.10	0.02	0.04	0.99	1.73	2.89
Middle Kittanning	all	I	234	1.33	1.78	1.18	0.01	0.99	1.63	2.39	6.85
Strasburg	all		11	2.53	3.12	1.54	0.38	2.74	3.11	3.95	5.48
Lower Kittanning Rider	all		7	0.39	0.68	0.71	0.07	0.16	0.49	1.06	1.78
Lower Kittanning/No 6 block	all	J	186	1.62	2.24	1.43	0.02	1.21	2.02	3.02	8.08
Clarion	all	K	74	1.58	2.15	1.33	0.03	1.39	1.98	2.68	7.31
Brookville	all	L	71	1.36	1.85	1.60	0.07	0.91	1.38	2.03	8.97
No 5 Block	all	M	55	0.23	0.69	0.93	0.01	0.05	0.33	0.84	3.46
Tionesta	all		5	3.00	3.77	2.92	1.13	2.02	3.39	3.65	8.67
Upper Mercer	all		8	2.63	2.89	1.28	1.31	2.20	2.59	4.00	4.66
Lower Mercer	all		22	1.00	1.64	1.30	0.02	0.80	1.01	2.58	4.75
Quakertown	all		9	0.93	1.80	2.18	0.14	0.44	1.11	1.52	6.81
Stockton	all	N	43	0.26	0.75	1.11	0.01	0.08	0.30	0.76	4.85
Coalburg	all	O	120	0.28	0.61	0.79	0.01	0.11	0.28	0.82	3.99
Winifrede/Hazard	all	P	63	0.19	0.45	0.68	0.01	0.07	0.20	0.58	3.66
Lower Winifrede/Hazard	all		10	0.16	0.30	0.38	0.04	0.07	0.15	0.33	1.16
Chilton/Taylor	all		14	0.50	1.01	1.08	0.07	0.19	0.37	2.17	2.86
Fire Clay Rider	all		23	0.92	1.58	1.27	0.03	0.57	1.30	2.31	4.21
Fire Clay	all	Q	62	0.24	0.49	0.66	0.02	0.10	0.22	0.56	3.33
Cedar Grove/Whitesburg	all	R *	22	0.76	1.39	1.11	0.02	0.38	1.08	2.37	3.54
Williamson/Amburgy	all	S	42	0.48	0.97	0.97	0.02	0.18	0.66	1.38	4.18
Campbell Creek/Upper Elkhorn No 3	all	T	80	0.30	0.76	0.94	0.03	0.09	0.24	1.22	3.50
Upper Elkhorn Nos 1 and 2/Powellton	all	U	90	0.36	0.93	1.17	0.01	0.12	0.30	1.46	5.17
Pond Creek	all	V	73	0.27	0.70	0.88	0.02	0.07	0.23	1.11	3.78
Matewan/Clintwood	all	W	123	0.36	0.85	1.06	0.01	0.14	0.32	1.23	5.22
Middle War Eagle/Eagle	all		17	0.43	0.83	0.71	0.02	0.18	0.68	1.35	2.06
Bens Creek/Blair	all		10	0.34	0.84	1.00	0.06	0.08	0.33	1.47	2.90
Little Eagle/Dorchester	all	X	85	0.28	0.47	0.56	0.01	0.15	0.31	0.51	3.27
Lower War Eagle/Hagy	all		9	0.51	0.91	0.94	0.06	0.23	0.59	1.13	2.80
Glenalum Tunnel/Splashdam	all	Y	34	0.18	0.66	1.07	0.01	0.04	0.18	0.61	4.20
Gilbert A/Upper Banner	all	Z	41	0.23	0.61	0.99	0.01	0.10	0.19	0.78	5.72
Gilbert/Lower Banner	all		17	0.18	0.29	0.34	0.03	0.09	0.17	0.30	1.36
Douglas/Kennedy	all	AA *	27	0.23	0.37	0.46	0.05	0.13	0.19	0.42	2.07
Jewell/Raven	all		19	0.20	0.56	0.98	0.03	0.07	0.18	0.37	3.61
Iaeger/Jawbone	all	BB *	29	0.17	0.55	0.94	0.02	0.07	0.10	0.29	3.23
Lower Iaeger/Tiller	all		16	0.60	2.16	2.40	0.03	0.07	1.27	3.72	7.62
Sewell B/Greasy Creek	all		4	0.78	0.86	0.46	0.48	0.55	0.74	1.06	1.49
Sewell A	all		0								
Sewell/Lower Seaboard	all	CC *	22	0.28	0.46	0.46	0.04	0.09	0.39	0.59	1.79
Welch/Upper Horsepen	all		8	0.13	0.21	0.18	0.01	0.09	0.14	0.37	0.46
Little Raleigh/Middle Horsepen	all		6	0.13	0.17	0.10	0.02	0.11	0.19	0.22	0.30
Beckley/War Creek	all	DD *	19	0.18	0.37	0.54	0.03	0.10	0.13	0.29	2.14
Fire Creek/Lower Horsepen	all		13	0.18	0.27	0.25	0.02	0.16	0.18	0.26	0.96
Pocahontas No 7	all		7	0.14	0.24	0.22	0.02	0.08	0.19	0.36	0.62
Pocahontas No 6	all		4	0.32	0.38	0.21	0.12	0.27	0.41	0.52	0.59
Pocahontas No 4	all		4	0.09	0.11	0.07	0.04	0.05	0.11	0.16	0.17
Pocahontas No 3	all	EE *	19	0.13	0.18	0.11	0.02	0.08	0.19	0.25	0.38

Table 4. Coal quality statistics for coal beds with≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4a. Coal Samples, all thicknesses.

Coal Bed Name This Study	Thickness range	Coal bed code N ≥ 30	N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quartile ppm	Maximum ppm
Waynesburg	all	A	60	16	19	14	0.80	10	15	25	74
Sewickley	all	B	42	5.4	6.7	4.1	0.80	3.7	6.1	8.5	19
Redstone	all	C	74	16	28	41	1.5	8.0	14	32	290
Pittsburgh Roof	all		9	11	17	12	0.85	9.3	14	25	41
Pittsburgh	all	D	136	11	17	18	0.70	5.5	11	22	87
Harlem	all		9	8.8	15	16	1.5	5.9	9.3	19	53
Lower Bakerstown	all	E	30	30	47	69	3.4	14	34	50	390
Brush Creek	all		11	21	32	23	0.76	16	30	40	77
Mahoning	all		20	71	96	87	9.3	46	73	110	410
Upper Freeport Rider	all		6	35	62	60	2.7	25	49	78	170
Upper Freeport	all	F	278	30	40	32	2.4	19	31	50	200
Lower Freeport	all	G	102	24	37	34	0.88	14	30	51	190
Upper Kittanning	all	H	67	24	41	41	1.0	12	29	53	230
Middle Kittanning Rider	all		8	22	43	39	1.4	16	38	61	120
Middle Kittanning	all	I	240	11	22	29	0.70	4.6	10	28	180
Strasburg	all		11	15	28	30	2.7	5.4	15	35	100
Lower Kittanning Rider	all		7	11	15	13	3.0	5.6	9.6	22	38
Lower Kittanning/No 6 block	all	J	197	15	27	40	0.31	8.3	15	32	320
Clarion	all	K	74	10	17	17	1.4	3.9	9.8	27	73
Brookville	all	L	73	10	20	31	0.49	4.9	10	18	180
No 5 Block	all	M	92	5.8	14	24	0.75	1.9	4.9	13	150
Tionesta	all		5	33	49	44	9.1	17	30	80	110
Upper Mercer	all		8	27	37	39	11	17	21	38	130
Lower Mercer	all		24	14	26	36	1.6	7.8	14	28	160
Quakertown	all		9	22	28	24	9.5	12	17	41	81
Stockton	all	N	62	5.2	12	16	0.60	1.7	4.3	20	79
Coalburg	all	O	142	6.8	15	25	0.40	2.6	6.2	16	170
Winifrede/Hazard	all	P	79	5.4	15	39	0.50	2.1	4.8	11	270
Lower Winifrede/Hazard	all		9	6.0	12	16	1.2	2.6	5.6	13	52
Chilton/Taylor	all		15	8.5	17	19	1.2	2.5	7.7	30	58
Fire Clay Rider	all		29	23	45	61	1.2	9.2	30	46	300
Fire Clay	all	Q	70	6.7	14	21	0.70	2.8	5.1	17	120
Cedar Grove/Whitesburg	all	R	39	10	24	46	0.75	3.6	10	34	280
Williamson/Amburgy	all	S	45	13	29	35	0.61	5.0	16	33	170
Campbell Creek/Upper Elkhorn No 3	all	T	142	7.2	17	26	0.85	2.3	7.0	19	170
Upper Elkhorn Nos 1 and 2/Powellton	all	U	114	13	42	90	0.80	4.3	11	34	680
Pond Creek	all	V	120	5.9	16	25	0.08	1.7	5.5	17	120
Matewan/Clintwood	all	W	126	10	26	37	0.50	3.4	9.9	32	180
Middle War Eagle/Eagle	all		23	17	38	37	1.1	3.8	29	66	110
Bens Creek/Blair	all		15	9.7	29	37	0.30	3.2	6.2	42	110
Little Eagle/Dorchester	all	X	88	12	23	28	1.1	3.9	14	29	130
Lower War Eagle/Hagy	all		13	23	75	110	1.0	4.2	48	59	330
Glenalum Tunnel/Splashdam	all	Y	35	7.7	21	31	0.87	2.8	5.7	22	120
Gilbert A/Upper Banner	all	Z	46	9.2	20	26	0.76	3.5	6.4	32	99
Gilbert/Lower Banner	all		23	11	23	34	1.6	4.0	8.4	22	120
Douglas/Kennedy	all	AA	37	14	23	25	1.6	7.7	11	30	100
Jewell/Raven	all		24	6.5	8.3	6.8	2.0	4.5	6.9	10	30
Iaeger/Jawbone	all	BB	34	5.9	14	20	0.45	2.4	6.0	15	80
Lower Iaeger/Tiller	all		17	15	50	81	1.6	4.7	14	56	310
Sewell B/Greasy Creek	all		6	23	39	32	1.5	20	29	66	79
Sewell A	all		7	3.8	5.3	6.1	2.0	2.4	3.1	4.3	19
Sewell/Lower Seaboard	all	CC	61	6.4	13	17	0.40	2.9	6.4	16	78
Welch/Upper Horsepen	all		15	12	22	22	1.4	4.5	11	40	64
Little Raleigh/Middle Horsepen	all		8	5.0	5.8	3.7	2.2	3.8	4.9	6.2	14
Beckley/War Creek	all	DD	30	8.8	18	22	0.25	4.2	12	19	89
Fire Creek/Lower Horsepen	all		22	7.9	12	11	1.3	3.1	12	16	40
Pocahontas No 7	all		7	12	26	31	2.7	4.6	7.6	44	75
Pocahontas No 6	all		12	11	18	22	1.4	6.4	11	19	85
Pocahontas No 4	all		13	6.6	12	13	1.2	3.5	5.0	16	39
Pocahontas No 3	all	EE	53	5.3	12	16	0.30	1.7	5.1	12	73

Table 4. Coal quality statistics for coal beds with≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4a. Coal Samples, all thicknesses.

				Mercury							
Coal Bed Name This Study	Thickness range	Coal bed code N ≥ 30	N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quartile ppm	Maximum ppm
Waynesburg	all	A	60	0.15	0.17	0.082	0.010	0.13	0.15	0.20	0.53
Sewickley	all	B	42	0.10	0.12	0.066	0.021	0.080	0.10	0.14	0.29
Redstone	all	C	74	0.15	0.22	0.17	0.007	0.10	0.17	0.29	0.93
Pittsburgh Roof	all		10	0.24	0.31	0.21	0.068	0.15	0.28	0.43	0.69
Pittsburgh	all	D	137	0.13	0.17	0.15	0.003	0.081	0.13	0.21	1.0
Harlem	all		9	0.076	0.14	0.11	0.007	0.030	0.18	0.23	0.31
Lower Bakerstown	all	E	30	0.16	0.23	0.24	0.003	0.12	0.18	0.25	1.3
Brush Creek	all		11	0.17	0.27	0.22	0.010	0.11	0.20	0.35	0.70
Mahoning	all		20	0.32	0.40	0.27	0.068	0.26	0.30	0.45	1.0
Upper Freeport Rider	all		6	0.76	0.84	0.44	0.490	0.57	0.73	0.83	1.7
Upper Freeport	all	F	278	0.25	0.33	0.25	0.003	0.20	0.29	0.38	2.9
Lower Freeport	all	G	103	0.20	0.30	0.24	0.003	0.14	0.27	0.41	1.6
Upper Kittanning	all	H	67	0.18	0.31	0.29	0.003	0.080	0.27	0.48	1.4
Middle Kittanning Rider	all		8	0.42	0.53	0.37	0.140	0.25	0.48	0.65	1.3
Middle Kittanning	all	I	243	0.15	0.23	0.21	0.003	0.11	0.17	0.28	1.6
Strasburg	all		11	0.23	0.27	0.13	0.076	0.17	0.27	0.38	0.45
Lower Kittanning Rider	all		7	0.048	0.12	0.12	0.003	0.037	0.090	0.18	0.33
Lower Kittanning/No 6 block	all	J	198	0.15	0.24	0.21	0.003	0.10	0.19	0.33	1.6
Clarion	all	K	74	0.14	0.18	0.14	0.010	0.086	0.13	0.24	0.76
Brookville	all	L	73	0.16	0.22	0.21	0.018	0.10	0.20	0.27	1.5
No 5 Block	all	M	93	0.13	0.18	0.18	0.023	0.082	0.14	0.23	1.5
Tionesta	all		5	0.11	0.16	0.16	0.054	0.055	0.057	0.18	0.43
Upper Mercer	all		8	0.16	0.21	0.14	0.040	0.11	0.20	0.29	0.42
Lower Mercer	all		24	0.13	0.23	0.17	0.003	0.088	0.20	0.39	0.51
Quakertown	all		9	0.12	0.16	0.13	0.033	0.073	0.12	0.26	0.42
Stockton	all	N	62	0.11	0.16	0.15	0.007	0.061	0.12	0.20	0.67
Coalburg	all	O	143	0.10	0.15	0.12	0.007	0.060	0.10	0.21	0.59
Winifrede/Hazard	all	P	79	0.090	0.16	0.17	0.007	0.042	0.084	0.22	1.0
Lower Winifrede/Hazard	all		9	0.044	0.079	0.093	0.007	0.020	0.049	0.055	0.26
Chilton/Taylor	all		15	0.15	0.20	0.17	0.043	0.090	0.16	0.26	0.74
Fire Clay Rider	all		29	0.19	0.23	0.16	0.055	0.12	0.18	0.26	0.72
Fire Clay	all	Q	70	0.082	0.12	0.099	0.007	0.050	0.080	0.22	0.43
Cedar Grove/Whitesburg	all	R	39	0.099	0.18	0.22	0.003	0.038	0.12	0.25	1.1
Williamson/Amburgy	all	S	45	0.092	0.14	0.11	0.010	0.045	0.091	0.22	0.49
Campbell Creek/Upper Elkhorn No 3	all	T	142	0.085	0.13	0.12	0.007	0.051	0.091	0.17	0.72
Upper Elkhorn Nos 1 and 2/Powellton	all	U	114	0.11	0.16	0.14	0.007	0.059	0.12	0.24	0.81
Pond Creek	all	V	121	0.078	0.12	0.12	0.003	0.049	0.080	0.16	0.57
Matewan/Clintwood	all	W	126	0.077	0.14	0.12	0.003	0.035	0.11	0.21	0.56
Middle War Eagle/Eagle	all		23	0.080	0.12	0.11	0.007	0.040	0.10	0.17	0.45
Bens Creek/Blair	all		15	0.052	0.10	0.11	0.007	0.025	0.039	0.18	0.29
Little Eagle/Dorchester	all	X	88	0.076	0.12	0.11	0.003	0.050	0.070	0.16	0.51
Lower War Eagle/Hagy	all		13	0.11	0.18	0.15	0.003	0.10	0.16	0.27	0.55
Glenalum Tunnel/Splashdam	all	Y	35	0.13	0.19	0.15	0.003	0.068	0.13	0.28	0.55
Gilbert A/Upper Banner	all	Z	46	0.058	0.099	0.11	0.003	0.050	0.070	0.12	0.51
Gilbert/Lower Banner	all		23	0.061	0.11	0.11	0.003	0.045	0.070	0.15	0.37
Douglas/Kennedy	all	AA	37	0.080	0.14	0.15	0.007	0.050	0.080	0.19	0.62
Jewell/Raven	all		24	0.080	0.10	0.083	0.015	0.050	0.075	0.13	0.37
Iaeger/Jawbone	all	BB	34	0.086	0.13	0.11	0.007	0.051	0.090	0.19	0.42
Lower Iaeger/Tiller	all		17	0.096	0.27	0.30	0.007	0.034	0.13	0.52	1.0
Sewell B/Greasy Creek	all		6	0.12	0.23	0.29	0.014	0.080	0.16	0.20	0.80
Sewell A	all		7	0.11	0.20	0.21	0.020	0.055	0.070	0.36	0.51
Sewell/Lower Seaboard	all	CC	61	0.13	0.20	0.21	0.017	0.060	0.14	0.26	0.97
Welch/Upper Horsepen	all		15	0.10	0.17	0.21	0.030	0.060	0.077	0.20	0.81
Little Raleigh/Middle Horsepen	all		8	0.083	0.11	0.080	0.014	0.064	0.091	0.13	0.27
Beckley/War Creek	all	DD	30	0.074	0.15	0.32	0.007	0.050	0.075	0.11	1.8
Fire Creek/Lower Horsepen	all		22	0.076	0.092	0.058	0.025	0.050	0.071	0.13	0.23
Pocahontas No 7	all		7	0.026	0.044	0.030	0.003	0.024	0.060	0.065	0.070
Pocahontas No 6	all		13	0.089	0.20	0.24	0.015	0.030	0.080	0.32	0.66
Pocahontas No 4	all		13	0.042	0.054	0.031	0.007	0.039	0.050	0.080	0.095
Pocahontas No 3	all	EE	53	0.068	0.11	0.12	0.007	0.050	0.072	0.11	0.66

Table 4. Coal quality statistics for coal beds with≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4a. Coal Samples, all thicknesses.

Coal Bed Name This Study	Thickness range	Coal bed code N ≥ 30	Manganese								
			N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quartile ppm	Maximum ppm
Waynesburg	all	A	60	26	32	27	10	20	25	35	180
Sewickley	all	B	42	20	33	53	6.4	11	16	24	260
Redstone	all	C	74	28	45	65	5	17	25	39	460
Pittsburgh Roof	all		10	14	15	5.9	6.1	13	14	17	27
Pittsburgh	all	D	137	21	29	33	1.4	14	20	35	300
Harlem	all		9	16	25	27	6.2	7.3	15	28	90
Lower Bakerstown	all	E	30	24	43	71	6.5	12	16	52	390
Brush Creek	all		11	13	27	46	3.4	5.6	8.6	25	160
Mahoning	all		20	12	16	13	3.3	6.4	13	25	59
Upper Freeport Rider	all		6	15	20	16	5.8	8.7	15	28	47
Upper Freeport	all	F	276	16	22	21	1.1	9.3	16	27	140
Lower Freeport	all	G	103	17	34	75	0.92	9.2	16	30	690
Upper Kittanning	all	H	67	13	18	22	3.3	8.2	12	21	170
Middle Kittanning Rider	all		8	24	26	12	14	16	24	32	46
Middle Kittanning	all	I	242	18	25	29	1.7	10	17	28	310
Strasburg	all		11	25	35	32	6.3	17	28	42	120
Lower Kittanning Rider	all		7	8.5	9.6	6.4	5.8	6.4	7.9	8.5	24
Lower Kittanning/No 6 block	all	J	198	16	26	47	1.6	9.7	15	26	430
Clarion	all	K	74	20	27	29	3.6	12	22	33	220
Brookville	all	L	73	17	29	57	2.1	10	17	26	470
No 5 Block	all	M	93	7.8	13	24	1.4	4.4	6.8	12	200
Tionesta	all		5	35	99	180	13	21	21	21	420
Upper Mercer	all		8	32	52	63	8.8	15	32	55	200
Lower Mercer	all		24	15	26	39	4.1	6.9	15	25	190
Quakertown	all		9	11	22	34	2.6	5.1	11	15	110
Stockton	all	N	62	7.6	11	18	1.2	5.3	7.1	12	140
Coalburg	all	O	143	9.4	13	13	1.1	5.9	9.0	16	120
Winifrede/Hazard	all	P	79	9.4	14	14	1.2	5.8	8.0	16	83
Lower Winifrede/Hazard	all		9	6.2	8.0	6.3	1.6	4.6	4.8	12	21
Chilton/Taylor	all		15	12	21	28	3	7.0	9.6	22	89
Fire Clay Rider	all		29	22	44	71	3.6	11	17	48	350
Fire Clay	all	Q	70	9.4	15	17	1.9	5.0	7.7	20	86
Cedar Grove/Whitesburg	all	R	39	11	41	130	0.73	5.1	9.4	15	660
Williamson/Amburgy	all	S	45	11	21	44	2.2	5.8	9.9	17	250
Campbell Creek/Upper Elkhorn No 3	all	T	142	7.8	11	11	1.2	3.9	7.4	15	63
Upper Elkhorn Nos 1 and 2/Powellton	all	U	114	7.7	12	15	0.96	4.2	7.1	12	110
Pond Creek	all	V	121	13	27	59	2.1	6.6	12	22	540
Matewan/Clintwood	all	W	126	8.0	15	38	1.1	4.4	7.1	14	390
Middle War Eagle/Eagle	all		23	9.6	21	28	0.75	4.7	8.0	19	100
Bens Creek/Blair	all		15	8.1	15	21	3	4.1	4.9	16	68
Little Eagle/Dorchester	all	X	88	9.0	17	28	1.1	3.8	8.3	15	170
Lower War Eagle/Hagy	all		13	13	22	31	2.4	6.3	12	24	120
Glenalum Tunnel/Splashdam	all	Y	35	7.8	14	18	1.2	4.0	6.0	18	84
Gilbert A/Upper Banner	all	Z	46	12	16	13	1.5	7.3	12	21	70
Gilbert/Lower Banner	all		23	20	25	17	4.5	14	17	29	60
Douglas/Kennedy	all	AA	37	18	32	39	2.8	9.0	20	33	190
Jewell/Raven	all		24	23	27	17	7.8	16	21	35	74
Iaeger/Jawbone	all	BB	34	15	26	32	1.1	7.5	16	31	160
Lower Iaeger/Tiller	all		17	24	29	18	7.3	15	29	37	74
Sewell B/Greasy Creek	all		6	14	22	29	5.4	7.9	12	16	81
Sewell A	all		7	16	27	30	2.4	11	17	28	91
Sewell/Lower Seaboard	all	CC	61	12	27	49	1.5	4.9	9.3	29	320
Welch/Upper Horsepen	all		15	9.4	11	6.7	3.8	6.1	9.4	15	27
Little Raleigh/Middle Horsepen	all		7	32	65	97	8.3	14	22	60	280
Beckley/War Creek	all	DD	30	11	36	77	1.4	4.8	7.2	27	320
Fire Creek/Lower Horsepen	all		22	6.7	11	15	1.0	3.1	7.5	13	75
Pocahontas No 7	all		7	15	27	29	1.3	8.8	18	37	79
Pocahontas No 6	all		13	8.3	19	37	1.5	2.9	8.0	15	140
Pocahontas No 4	all		13	18	37	68	3.4	8.5	21	30	260
Pocahontas No 3	all	EE	53	16	24	28	1.7	10	19	27	200

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4b. Thick Coal Samples, ≥28 inch thick.

				Selenium							
Coal bed name, this study	Thickness range	Coal bed code N≥30	N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quartile ppm	Maximum ppm
Waynesburg	≥ 28 in	A	56	2.7	2.8	0.89	0.64	2.4	2.9	3.3	5.5
Sewickley	≥ 28 in	B	40	2.6	2.9	1.3	0.70	2.2	2.6	3.6	7.2
Redstone	≥ 28 in	C	56	1.9	2.1	1.1	0.50	1.4	1.9	2.4	6.9
Pittsburgh	≥ 28 in	D	132	1.4	1.7	1.2	0.20	1.0	1.4	2.0	7.5
Lower Bakerstown	≥ 28 in		12	3.5	3.7	1.5	1.6	2.8	3.4	4.8	6.6
Mahoning	≥ 28 in		6	2.5	2.8	1.2	1.5	1.9	2.3	3.7	4.5
Upper Freeport	≥ 28 in	F	215	2.3	2.7	1.8	0.72	1.7	2.2	3.0	14
Lower Freeport	≥ 28 in	G	66	3.5	4.2	2.9	1.1	2.3	3.2	4.9	15
Upper Kittanning	≥ 28 in	H	32	4.5	5.2	3.1	1.4	2.8	4.1	6.4	13
Middle Kittanning	≥ 28 in	I	168	3.3	3.6	2.0	0.99	2.3	3.2	4.5	17
Lower Kittanning/No 6 block	≥ 28 in	J	141	3.4	4.0	2.6	0.60	2.2	3.7	5.4	20
Clarion	≥ 28 in	K	47	6.0	6.5	2.5	2.3	5.0	6.2	7.5	14
Brookville	≥ 28 in	L	30	5.4	6.1	3.0	1.8	3.9	5.3	7.7	14
No 5 Block	≥ 28 in	M	65	7.0	7.4	2.6	3.1	5.7	7.0	8.9	17
Lower Mercer	≥ 28 in		7	7.7	8.3	3.3	4.0	5.9	8.3	10	13
Stockton	≥ 28 in	N	51	5.3	5.6	1.9	2.7	4.1	5.5	7.1	11
Coalburg	≥ 28 in	O	67	5.0	5.2	1.5	1.8	4.3	4.9	6.3	8.7
Winifrede/Hazard	≥ 28 in	P	48	4.7	4.9	1.7	2.4	3.8	4.8	5.6	11
Chilton/Taylor	≥ 28 in		9	2.5	3.0	1.7	0.73	2.0	3.0	3.8	5.8
Fire Clay Rider	≥ 28 in		13	4.0	4.1	1.3	2.4	3.5	3.6	4.4	7.8
Fire Clay	≥ 28 in	Q	40	3.5	3.7	1.2	1.3	2.8	3.4	4.5	6.3
Cedar Grove/Whitesburg	≥ 28 in		16	3.5	3.6	1.1	2.2	2.5	3.7	4.5	5.5
Williamson/Amburgy	≥ 28 in		19	3.1	3.5	1.7	0.90	2.5	3.5	4.1	7.5
Campbell Creek/Upper Elkhorn No 3	≥ 28 in	T	80	3.8	4.0	1.3	1.7	3.0	3.9	4.7	7.8
Upper Elkhorn Nos 1 and 2/Powellton	≥ 28 in	U	59	3.4	3.7	1.5	0.93	2.9	3.6	4.4	7.7
Pond Creek	≥ 28 in	V	78	3.5	3.7	1.2	1.6	2.7	3.7	4.5	6.7
Matewan/Clintwood	≥ 28 in	W	54	2.8	3.2	1.6	0.54	2.1	2.9	3.8	7.4
Middle War Eagle/Eagle	≥ 28 in		12	3.4	3.7	1.4	1.7	3.0	3.4	4.3	6.0
Bens Creek/Blair	≥ 28 in		11	2.1	2.1	0.55	1.1	1.9	2.0	2.4	3.3
Lit le Eagle/Dorchester	≥ 28 in	X	53	2.7	3.0	1.6	1.2	1.8	2.5	3.5	7.1
Lower War Eagle/Hagy	≥ 28 in		8	2.9	3.0	0.86	1.3	2.7	3.1	3.7	4.0
Glenalum Tunnel/Splashdam	≥ 28 in		17	2.6	2.8	0.93	0.76	2.2	2.8	3.2	4.4
Gilbert A/Upper Banner	≥ 28 in		24	3.1	3.3	1.1	1.2	2.5	3.0	3.6	5.6
Gilbert/Lower Banner	≥ 28 in		17	2.7	2.9	1.1	1.7	2.2	2.7	3.0	6.3
Douglas/Kennedy	≥ 28 in		22	1.7	2.2	2.2	0.40	1.1	1.3	2.3	11
Jewell/Raven	≥ 28 in		19	1.7	2.0	0.88	0.20	1.5	2.0	2.7	3.8
Iaeger/Jawbone	≥ 28 in		17	1.9	2.5	1.3	0.07	1.7	2.7	3.1	4.8
Lower Iaeger/Tiller	≥ 28 in		7	2.6	2.8	0.97	1.0	2.8	2.9	3.0	4.3
Sewell/Lower Seaboard	≥ 28 in	CC	41	2.0	2.5	2.3	0.76	1.3	1.8	2.5	14
Welch/Upper Horsepen	≥ 28 in		10	1.6	1.8	0.91	0.70	1.1	1.7	2.2	3.6
Lit le Raleigh/Middle Horsepen	≥ 28 in		5	2.2	2.2	0.44	1.7	1.9	2.1	2.6	2.7
Beckley/War Creek	≥ 28 in		18	1.5	1.6	0.44	0.78	1.3	1.5	1.8	2.4
Fire Creek/Lower Horsepen	≥ 28 in		14	2.5	2.7	1.1	1.1	1.8	2.8	3.3	4.9
Pocahontas No 6	≥ 28 in		10	2.7	2.9	1.4	1.4	2.1	2.5	3.8	5.9
Pocahontas No 4	≥ 28 in		13	2.4	2.5	1.1	1.8	2.0	2.3	2.5	5.9
Pocahontas No 3	≥ 28 in	EE	43	3.0	3.4	1.7	1.1	2.3	3.0	4.1	8.2

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4b. Thick Coal Samples, ≥28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	Thickness							
			N	Geometric mean in	Average in	Standard Deviation in	Minimum in	Lower Quartile in	Median in	Upper Quartile in	Maximum in
Waynesburg	≥ 28 in	A	56	47.3	49.8	16.7	28.3	37.3	46.1	58.4	95.0
Sewickley	≥ 28 in	B	40	46.4	47.5	11.2	32.0	39.0	47.8	55.1	87.5
Redstone	≥ 28 in	C	56	51.6	54.0	15.7	28.0	38.1	55.1	67.2	88.0
Pittsburgh	≥ 28 in	D	132	60.0	63.3	20.7	28.0	49.9	60.5	75.5	125 0
Lower Bakerstown	≥ 28 in		12	36.1	36.8	8.0	28.0	32.1	35.9	36.9	56.0
Mahoning	≥ 28 in		6	37.2	38.5	12.4	28.0	33.2	34.8	37.1	63.0
Upper Freeport	≥ 28 in	F	215	46.2	48.1	14.4	28.0	39.0	46.5	50.5	105 5
Lower Freeport	≥ 28 in	G	67	41.3	43.0	13.2	28.5	33.6	38.0	50.2	74.0
Upper Kittanning	≥ 28 in	H	32	41.0	43.2	15.5	28.4	31.4	37.2	51.8	94.8
Middle Kittanning	≥ 28 in	I	168	39.4	40.4	10.3	28.0	33.5	38.7	45.0	95.5
Lower Kittanning/No 6 block	≥ 28 in	J	141	37.9	38.9	10.2	28.0	32.4	36.0	41.5	86.4
Clarion	≥ 28 in	K	47	41.1	43.0	14.5	28.8	31.9	39.3	48.8	96.0
Brookville	≥ 28 in	L	30	39.7	40.9	10.4	28.4	32.3	37.8	49.4	61.5
No 5 Block	≥ 28 in	M	65	53.8	59.7	30.9	28.0	40.0	49.6	70.5	171 8
Lower Mercer	≥ 28 in		7	38.9	40.5	13.8	29.4	33.6	35.1	41.1	69.6
Stockton	≥ 28 in	N	51	47.7	49.7	14.5	28.5	40.0	48.0	58.7	93.3
Coalburg	≥ 28 in	O	67	47.0	49.7	18.1	28.0	37.0	45.5	55.6	112 5
Winifrede/Hazard	≥ 28 in	P	48	40.0	41.5	12.1	28.0	32.8	37.9	45.9	73.2
Chilton/Taylor	≥ 28 in		9	43.1	45.6	17.8	29.6	35.0	40.9	46.1	85.2
Fire Clay Rider	≥ 28 in		13	42.6	44.6	16.3	33.0	35.0	38.0	46.0	91.3
Fire Clay	≥ 28 in	Q	40	43.7	45.3	13.0	28.0	34.7	43.0	51.3	80.5
Cedar Grove/Whitesburg	≥ 28 in		16	38.6	39.4	8.1	28.3	31.8	40.4	45.3	52.0
Williamson/Amburgy	≥ 28 in		19	41.3	42.9	13.4	28.8	35.2	39.4	46.6	84.0
Campbell Creek/Upper Elkhorn No 3	≥ 28 in	T	80	38.4	39.7	11.2	28.0	31.3	37.6	44.8	85.5
Upper Elkhorn Nos 1 and 2/Powellton	≥ 28 in	U	59	39.0	40.0	9.2	28.0	32.6	39.0	43.9	69.3
Pond Creek	≥ 28 in	V	78	42.7	44.3	12.8	28.0	35.1	42.1	47.4	85.4
Matewan/Clintwood	≥ 28 in	W	54	36.9	37.9	10.2	28.0	31.2	35.5	43.2	87.2
Middle War Eagle/Eagle	≥ 28 in		12	38.6	39.7	10.3	28.8	34.2	37.8	39.0	64.8
Bens Creek/Blair	≥ 28 in		11	35.2	35.8	7.1	28.5	30.9	32.0	39.4	50.0
Lit le Eagle/Dorchester	≥ 28 in	X	54	37.7	38.5	8.6	28.7	33.1	36.5	41.9	66.0
Lower War Eagle/Hagy	≥ 28 in		8	33.4	33.6	3.7	28.4	32.0	33.5	36.1	39.0
Glenalum Tunnel/Splashdam	≥ 28 in		17	41.5	42.8	11.1	28.8	32.0	41.4	49.6	69.0
Gilbert A/Upper Banner	≥ 28 in		24	39.5	41.7	17.4	29.4	32.1	36.8	42.5	110 2
Gilbert/Lower Banner	≥ 28 in		17	46.3	47.4	11.2	32.8	39.6	44.4	56.4	71.0
Douglas/Kennedy	≥ 28 in		22	36.8	37.7	8.8	28.0	32.3	35.0	40.4	62.0
Jewell/Raven	≥ 28 in		19	40.5	41.7	10.8	28.0	32.8	41.0	47.2	68.4
Iaeger/Jawbone	≥ 28 in		17	44.2	46.2	14.5	29.5	35.0	41.2	59.9	77.8
Lower Iaeger/Tiller	≥ 28 in		7	40.0	41.5	13.6	29.8	34.3	36.0	44.0	68.4
Sewell/Lower Seaboard	≥ 28 in	CC	41	42.4	43.7	11.2	28.6	35.9	42.8	52.0	70.6
Welch/Upper Horsepen	≥ 28 in		10	45.1	51.4	31.8	28.0	31.3	38.0	57.8	128 0
Lit le Raleigh/Middle Horsepen	≥ 28 in		5	43.7	43.8	4.0	42.0	42.0	42.0	42.0	51.0
Beckley/War Creek	≥ 28 in		18	40.5	42.8	16.0	28.0	30.5	39.3	51.0	87.0
Fire Creek/Lower Horsepen	≥ 28 in		14	41.4	43.2	13.6	29.5	32.3	36.8	56.3	70.0
Pocahontas No 6	≥ 28 in		10	35.5	35.8	4.8	30.1	31.1	35.8	39.9	43.5
Pocahontas No 4	≥ 28 in		13	64.8	65.9	12.6	49.0	60.1	62.6	76.0	91.0
Pocahontas No 3	≥ 28 in	EE	43	50.5	52.1	14.0	31.0	43.3	51.8	57.6	94.0

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4b. Thick Coal Samples, ≥28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	N	Ash Yield Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quartile percent	Maximum percent
Waynesburg	≥ 28 in	A	53	16.61	17.12	3.34	3.16	15.66	17.16	19.37	22.96
Sewickley	≥ 28 in	B	38	11.42	11.81	3.06	5.70	9.71	11.31	13.23	20.20
Redstone	≥ 28 in	C	53	9.51	10.20	4.39	5.60	7.60	9.02	11.10	25.70
Pittsburgh	≥ 28 in	D	124	9.98	10.51	3.88	4.40	8.03	10.10	11.74	32.03
Lower Bakerstown	≥ 28 in		11	11.84	13.25	6.49	5.55	8.07	11.83	17.37	24.90
Mahoning	≥ 28 in		4	11.31	11.45	2.09	9.51	10.08	11.02	12.39	14.25
Upper Freeport	≥ 28 in	F	169	12.44	13.22	4.79	3.60	10.30	12.00	15.60	29.10
Lower Freeport	≥ 28 in	G	67	9.23	9.94	4.12	3.90	7.67	8.46	11.41	26.43
Upper Kittanning	≥ 28 in	H	30	11.35	11.82	3.56	5.69	10.22	11.20	12.98	24.00
Middle Kittanning	≥ 28 in	I	165	9.41	10.59	5.07	2.20	6.80	9.20	14.32	23.80
Lower Kittanning/No 6 block	≥ 28 in	J	138	10.45	11.44	5.13	2.80	7.70	10.55	13.49	31.50
Clarion	≥ 28 in	K	47	13.40	14.37	5.40	4.80	10.81	13.58	17.25	28.38
Brookville	≥ 28 in	L *	29	12.08	13.10	5.83	6.22	8.90	11.33	14.62	29.45
No 5 Block	≥ 28 in	M	58	10.37	11.31	4.70	2.70	7.90	10.36	14.09	27.50
Lower Mercer	≥ 28 in		7	15.02	15.68	5.49	10.82	12.78	13.42	16.43	27.09
Stockton	≥ 28 in	N	49	11.33	12.57	5.62	4.22	8.00	12.65	15.43	28.20
Coalburg	≥ 28 in	O	67	11.28	12.35	5.36	3.42	8.70	11.40	14.32	30.70
Winifrede/Hazard	≥ 28 in	P	46	9.27	10.72	5.65	2.44	6.91	9.75	14.35	28.50
Chilton/Taylor	≥ 28 in		9	11.19	11.49	2.59	6.80	9.20	12.70	13.28	14.00
Fire Clay Rider	≥ 28 in		13	11.58	12.24	4.35	6.51	9.00	11.12	15.90	22.00
Fire Clay	≥ 28 in	Q	40	10.15	11.45	5.83	3.34	7.06	10.50	14.62	31.80
Cedar Grove/Whitesburg	≥ 28 in		15	9.15	10.50	5.60	2.47	7.45	9.80	11.90	23.30
Williamson/Amburgy	≥ 28 in		19	7.57	8.92	5.43	2.30	6.26	7.63	11.09	26.10
Campbell Creek/Upper Elkhorn No 3	≥ 28 in	T	79	6.89	7.60	3.43	2.30	4.88	7.17	9.30	21.60
Upper Elkhorn Nos 1 and 2/Powellton	≥ 28 in	U	59	6.20	6.97	3.55	1.65	4.56	6.24	8.89	19.10
Pond Creek	≥ 28 in	V	78	7.11	8.00	3.73	1.66	5.48	7.24	10.27	16.80
Matewan/Clintwood	≥ 28 in	W	54	6.02	6.68	3.46	2.57	4.51	6.05	7.45	21.60
Middle War Eagle/Eagle	≥ 28 in		10	4.85	5.55	3.23	2.10	3.67	3.80	7.25	12.54
Bens Creek/Blair	≥ 28 in		11	4.23	6.07	6.13	1.60	2.65	3.22	5.90	18.30
Lit le Eagle/Dorchester	≥ 28 in	X	54	7.19	8.75	5.82	1.93	4.75	6.53	12.05	28.20
Lower War Eagle/Hagy	≥ 28 in		8	9.68	11.03	6.01	4.30	8.52	9.99	11.89	22.80
Glenalum Tunnel/Splashdam	≥ 28 in		17	8.98	10.50	6.29	3.40	6.10	9.10	13.90	25.30
Gilbert A/Upper Banner	≥ 28 in		22	7.34	7.94	3.50	3.60	5.99	6.72	9.38	18.19
Gilbert/Lower Banner	≥ 28 in		14	10.95	11.86	4.68	4.68	7.75	11.85	14.70	19.63
Douglas/Kennedy	≥ 28 in		18	6.34	7.40	4.95	3.08	4.57	6.25	8.25	22.57
Jewell/Raven	≥ 28 in		16	6.20	7.81	5.95	2.40	3.75	5.86	9.35	24.59
Iaeger/Jawbone	≥ 28 in		16	11.51	13.83	8.38	2.44	7.88	12.80	16.46	30.90
Lower Iaeger/Tiller	≥ 28 in		7	7.77	8.63	4.34	3.68	6.05	7.20	10.51	16.40
Sewell/Lower Seaboard	≥ 28 in	CC	37	5.05	5.57	2.62	2.30	3.60	4.44	7 00	12.36
Welch/Upper Horsepen	≥ 28 in		7	6.71	7.45	3.54	3.40	4.55	8.00	9.22	13.19
Lit le Raleigh/Middle Horsepen	≥ 28 in		5	6.94	7.14	1.90	5.10	5.80	6.50	9.10	9.20
Beckley/War Creek	≥ 28 in		16	5.78	6.62	3.01	0.90	5.05	6.30	7.53	12.00
Fire Creek/Lower Horsepen	≥ 28 in		14	6.92	7.54	3.53	3.60	5.43	6.50	8.90	17.20
Pocahontas No 6	≥ 28 in		10	7.71	8.46	4.14	4.60	5.60	6.95	10.58	17.90
Pocahontas No 4	≥ 28 in		13	6.14	6.35	1.84	4.20	5.60	5.93	6.60	11.40
Pocahontas No 3	≥ 28 in	EE	41	7.62	8.44	3.85	2.90	5.80	7.30	10.60	16.09

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4b. Thick Coal Samples, ≥28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	N	Sulfur Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quartile percent	Maximum percent
Waynesburg	≥ 28 in	A	54	2.59	2.75	0.93	0.70	2.20	2.65	3 34	5.20
Sewickley	≥ 28 in	B	38	2.58	2.89	1.29	0.70	1.95	2.92	3 58	5.90
Redstone	≥ 28 in	C	53	2.59	2.76	0.99	0.90	2.10	2.60	3.20	5.66
Pittsburgh	≥ 28 in	D	124	2.92	3.34	1.50	0.40	2.08	3.35	4.50	6.70
Lower Bakerstown	≥ 28 in		11	1.91	2.23	1.11	0.40	1.55	2.40	2.91	4.39
Mahoning	≥ 28 in		4	2.22	2.73	1.50	0.63	2.26	3.06	3.53	4.15
Upper Freeport	≥ 28 in	F	210	2.11	2.35	1.12	0.59	1.60	2.13	2.80	6.30
Lower Freeport	≥ 28 in	G	67	2.11	2.49	1.25	0.50	1.68	2.56	3.23	5.75
Upper Kittanning	≥ 28 in	H	30	1.99	2.35	1.22	0.40	1.36	2.25	3.30	5.60
Middle Kittanning	≥ 28 in	I	165	2.87	3.18	1.32	0.50	2.30	3.05	3.91	7.50
Lower Kittanning/No 6 block	≥ 28 in	J	138	2.88	3.42	1.78	0.40	2.11	3.30	4.55	8.43
Clarion	≥ 28 in	K	47	3.30	3.71	1.66	0.66	2.70	3.70	4.46	9.34
Brookville	≥ 28 in	L *	29	3.37	3.76	1.96	1.31	2.30	3.12	4.56	10.40
No 5 Block	≥ 28 in	M	58	0.81	0.92	0.66	0.40	0.60	0.73	0 97	4.87
Lower Mercer	≥ 28 in		7	2.37	2.89	2.07	1.36	1.47	1.60	4.08	6.15
Stockton	≥ 28 in	N	49	0.94	1.17	1.01	0.50	0.60	0.70	1.30	5.40
Coalburg	≥ 28 in	O	67	0.89	0.99	0.54	0.40	0.67	0.80	1.10	3.12
Winifrede/Hazard	≥ 28 in	P	46	0.89	0.99	0.55	0.50	0.65	0.80	1 08	3.50
Chilton/Taylor	≥ 28 in		9	1.15	1.28	0.72	0.60	0.90	1.11	1.32	3.10
Fire Clay Rider	≥ 28 in		13	2.19	2.63	1.45	0.69	1.44	2.80	3.50	5.20
Fire Clay	≥ 28 in	Q	40	0.94	1.02	0.48	0.50	0.74	0.86	1.11	2.57
Cedar Grove/Whitesburg	≥ 28 in		15	1.01	1.19	0.97	0.60	0.77	0.90	1.15	4.53
Williamson/Amburgy	≥ 28 in		19	1.32	1.61	1.05	0.59	0.78	1.16	2.45	4.00
Campbell Creek/Upper Elkhorn No 3	≥ 28 in	T	79	1.09	1.28	0.82	0.46	0.70	0.90	1.65	4.00
Upper Elkhorn Nos 1 and 2/Powellton	≥ 28 in	U	59	1.03	1.21	0.86	0.51	0.70	0.80	1.39	4.50
Pond Creek	≥ 28 in	V	78	0.94	1.11	0.78	0.41	0.60	0.80	1 32	4.50
Matewan/Clintwood	≥ 28 in	W	54	1.12	1.33	0.90	0.50	0.71	0.92	1.72	4.40
Middle War Eagle/Eagle	≥ 28 in		10	1.13	1.38	0.88	0.46	0.62	1.20	2.13	2.80
Bens Creek/Blair	≥ 28 in		11	1.15	1.31	0.73	0.50	0.80	1.00	1.88	2.60
Lit le Eagle/Dorchester	≥ 28 in	X	54	1.07	1.16	0.55	0.60	0.81	1.00	1 28	3.38
Lower War Eagle/Hagy	≥ 28 in		8	1.38	1.58	0.86	0.60	0.87	1.41	2.17	3.00
Glenalum Tunnel/Splashdam	≥ 28 in		17	1.01	1.28	1.16	0.60	0.66	0.75	1.16	4.40
Gilbert A/Upper Banner	≥ 28 in		22	0.96	1.17	0.81	0.40	0.60	0.82	1.79	3.17
Gilbert/Lower Banner	≥ 28 in		14	0.85	0.93	0.45	0.56	0.60	0.80	1.04	2.10
Douglas/Kennedy	≥ 28 in		18	0.84	0.91	0.40	0.50	0.60	0.77	0.93	1.70
Jewell/Raven	≥ 28 in		16	0.87	1.16	1.20	0.50	0.58	0.72	0.95	4.20
Iaeger/Jawbone	≥ 28 in		16	0.61	0.62	0.11	0.50	0.54	0.60	0.64	0.90
Lower Iaeger/Tiller	≥ 28 in		7	1.03	1.82	2.36	0.50	0.53	0.60	1.93	6.70
Sewell/Lower Seaboard	≥ 28 in	CC	37	0.81	0.87	0.36	0.40	0.60	0.80	1 00	2.20
Welch/Upper Horsepen	≥ 28 in		7	0.77	0.82	0.31	0.50	0.61	0.80	0.90	1.40
Lit le Raleigh/Middle Horsepen	≥ 28 in		5	0.78	0.80	0.19	0.50	0.80	0.80	0.90	1.00
Beckley/War Creek	≥ 28 in		16	0.95	1.06	0.49	0.40	0.60	1.15	1.43	1.90
Fire Creek/Lower Horsepen	≥ 28 in		14	0.89	0.94	0.31	0.40	0.73	0.85	1.18	1.50
Pocahontas No 6	≥ 28 in		10	0.97	0.99	0.19	0.80	0.82	0.90	1.18	1.30
Pocahontas No 4	≥ 28 in		13	0.64	0.65	0.12	0.50	0.60	0.65	0.70	0.88
Pocahontas No 3	≥ 28 in	EE	41	0.69	0.73	0.28	0.40	0.52	0.65	0.80	1.80

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4b. Thick Coal Samples, ≥28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	Pyritic Sulfur							
			N	Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quartile percent	Maximum percent
Waynesburg	≥ 28 in	A	47	1.57	1.83	0.89	0.14	1.12	1.78	2 33	4.00
Sewickley	≥ 28 in	B	36	1.05	1.40	0.76	0.02	0.91	1.30	1 93	2.87
Redstone	≥ 28 in	C *	19	1.76	1.97	1.03	0.67	1.30	1.75	2.31	4.93
Pittsburgh	≥ 28 in	D	94	1.64	2.08	1.09	0.05	1.33	2.00	2.89	5.16
Lower Bakerstown	≥ 28 in		11	0.84	1.37	0.84	0.01	0.65	1.65	1.76	2.73
Mahoning	≥ 28 in		4	0.64	1.58	1.14	0.02	1.18	1.79	2.18	2.72
Upper Freeport	≥ 28 in	F	208	1.19	1.52	1.00	0.05	0.86	1.33	1.81	5.57
Lower Freeport	≥ 28 in	G	66	0.97	1.58	1.04	0.01	0.73	1.59	2.31	3.92
Upper Kittanning	≥ 28 in	H *	29	0.94	1.57	1.20	0.02	0.66	1.43	2.15	5.41
Middle Kittanning	≥ 28 in	I	161	1.46	1.80	1.03	0.04	1.07	1.69	2.27	6.49
Lower Kittanning/No 6 block	≥ 28 in	J	134	1.54	2.19	1.42	0.02	1.16	2.01	3.00	6.07
Clarion	≥ 28 in	K	47	1.76	2.19	1.38	0.18	1.34	1.99	2.66	7.31
Brookville	≥ 28 in	L *	29	1.99	2.44	1.82	0.63	1.32	1.75	3.10	8.97
No 5 Block	≥ 28 in	M	31	0.13	0.38	0.66	0.02	0.03	0.10	0 39	3.07
Lower Mercer	≥ 28 in		6	1.18	1.59	1.59	0.58	0.75	0.92	1.47	4.75
Stockton	≥ 28 in	N	35	0.23	0.60	0.88	0.01	0.09	0.30	0.68	4.02
Coalburg	≥ 28 in	O	51	0.24	0.42	0.45	0.03	0.11	0.27	0.53	1.79
Winifrede/Hazard	≥ 28 in	P	34	0.20	0.41	0.56	0.01	0.07	0.24	0 54	2.95
Chilton/Taylor	≥ 28 in		9	0.31	0.46	0.58	0.13	0.18	0.33	0.38	1.97
Fire Clay Rider	≥ 28 in		13	0.81	1.35	1.00	0.03	0.62	1.19	1.96	3.41
Fire Clay	≥ 28 in	Q	36	0.23	0.39	0.44	0.03	0.12	0.21	0.47	1.85
Cedar Grove/Whitesburg	≥ 28 in		6	0.24	0.77	1.15	0.02	0.07	0.34	0.79	3.02
Williamson/Amburgy	≥ 28 in		19	0.39	0.85	0.93	0.04	0.12	0.35	1.27	3.34
Campbell Creek/Upper Elkhorn No 3	≥ 28 in	T	43	0.29	0.68	0.84	0.03	0.10	0.22	1.14	2.92
Upper Elkhorn Nos 1 and 2/Powellton	≥ 28 in	U	42	0.23	0.52	0.74	0.02	0.09	0.19	0.76	3.65
Pond Creek	≥ 28 in	V	40	0.19	0.36	0.40	0.02	0.06	0.17	0 56	1.39
Matewan/Clintwood	≥ 28 in	W	53	0.29	0.59	0.72	0.03	0.12	0.26	0.84	3.30
Middle War Eagle/Eagle	≥ 28 in		7	0.23	0.61	0.69	0.02	0.08	0.18	1.13	1.65
Bens Creek/Blair	≥ 28 in		7	0.32	0.73	0.79	0.06	0.07	0.42	1.30	1.93
Lit le Eagle/Dorchester	≥ 28 in	X	51	0.25	0.40	0.38	0.01	0.14	0.33	0 50	2.12
Lower War Eagle/Hagy	≥ 28 in		5	0.31	0.50	0.43	0.06	0.12	0.59	0.60	1.13
Glenalum Tunnel/Splashdam	≥ 28 in		16	0.16	0.66	1.17	0.01	0.03	0.20	0.59	4.20
Gilbert A/Upper Banner	≥ 28 in		22	0.21	0.47	0.60	0.02	0.09	0.15	0.76	1.91
Gilbert/Lower Banner	≥ 28 in		12	0.14	0.18	0.16	0.03	0.09	0.14	0.21	0.65
Douglas/Kennedy	≥ 28 in		15	0.19	0.26	0.26	0.06	0.12	0.19	0.27	1.08
Jewell/Raven	≥ 28 in		16	0.17	0.42	0.70	0.03	0.06	0.14	0.36	2.20
Iaeger/Jawbone	≥ 28 in		14	0.10	0.13	0.10	0.02	0.06	0.10	0.14	0.36
Lower Iaeger/Tiller	≥ 28 in		6	0.17	1.21	2.17	0.03	0.04	0.05	1.27	5.43
Sewell/Lower Seaboard	≥ 28 in	CC *	10	0.19	0.30	0.30	0.04	0.08	0.18	0.46	1.00
Welch/Upper Horsepen	≥ 28 in		6	0.16	0.21	0.16	0.08	0.09	0.14	0.30	0.45
Lit le Raleigh/Middle Horsepen	≥ 28 in		5	0.18	0.20	0.08	0.08	0.19	0.19	0.23	0.30
Beckley/War Creek	≥ 28 in		10	0.20	0.39	0.43	0.04	0.09	0.18	0.72	1.12
Fire Creek/Lower Horsepen	≥ 28 in		7	0.22	0.32	0.31	0.04	0.18	0.19	0.35	0.96
Pocahontas No 6	≥ 28 in		2	0.40	0.41	0.12	0.32	na	na	na	0.49
Pocahontas No 4	≥ 28 in		4	0.09	0.11	0.07	0.04	0.05	0.11	0.16	0.17
Pocahontas No 3	≥ 28 in	EE *	18	0.13	0.17	0.11	0.02	0.08	0.18	0.26	0.38

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4b. Thick Coal Samples, ≥28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	Arsenic								
			N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quartile ppm	Maximum ppm
Waynesburg	≥ 28 in	A	56	16	19	12	5.8	11	15	23	74
Sewickley	≥ 28 in	B	40	5.2	6.4	4.0	0.80	3.6	5.6	7.6	19
Redstone	≥ 28 in	C	56	14	23	25	2.7	7.9	12	26	120
Pittsburgh	≥ 28 in	D	131	11	17	17	0.70	5.3	11	22	87
Lower Bakerstown	≥ 28 in		12	20	28	23	3.4	13	17	43	73
Mahoning	≥ 28 in		6	55	76	53	9.3	44	75	95	160
Upper Freeport	≥ 28 in	F	215	28	36	29	2.4	18	29	44	200
Lower Freeport	≥ 28 in	G	67	22	33	33	0.88	12	28	38	190
Upper Kittanning	≥ 28 in	H	32	23	34	29	2.4	14	27	44	130
Middle Kittanning	≥ 28 in	I	168	9.3	17	23	0.90	4.3	8.3	20	180
Lower Kittanning/No 6 block	≥ 28 in	J	140	13	21	32	0.31	7.8	14	26	320
Clarion	≥ 28 in	K	47	8.9	15	17	2.1	3.9	6.3	21	61
Brookville	≥ 28 in	L	30	10	19	33	2.3	6.7	8.1	18	180
No 5 Block	≥ 28 in	M	65	4.5	8.6	11	0.75	1.8	4.3	10	49
Lower Mercer	≥ 28 in		7	18	25	27	5.7	13	14	23	84
Stockton	≥ 28 in	N	51	4.6	10	14	0.60	1.7	3.7	14	79
Coalburg	≥ 28 in	O	67	5.7	11	20	0.60	2.2	5.8	14	150
Winifrede/Hazard	≥ 28 in	P	48	5.6	11	18	0.70	2.5	4.7	12	100
Chilton/Taylor	≥ 28 in		9	7.2	12	12	1.5	2.6	7.7	15	31
Fire Clay Rider	≥ 28 in		13	14	20	15	1.2	9.1	18	30	47
Fire Clay	≥ 28 in	Q	40	6.3	12	20	0.70	3.0	5.1	15	120
Cedar Grove/Whitesburg	≥ 28 in		16	5.9	11	14	0.75	1.7	7.8	9.8	42
Williamson/Amburgy	≥ 28 in		19	9.3	24	35	0.80	3.6	10	23	120
Campbell Creek/Upper Elkhorn No 3	≥ 28 in	T	80	6.7	13	18	0.85	2.3	7.1	14	85
Upper Elkhorn Nos 1 and 2/Powellton	≥ 28 in	U	59	7.4	16	26	0.80	3.5	7.7	16	160
Pond Creek	≥ 28 in	V	77	3.6	7.7	11	0.08	1.4	3.2	8.5	48
Matewan/Clintwood	≥ 28 in	W	54	8.3	19	32	0.90	3.4	7.2	24	160
Middle War Eagle/Eagle	≥ 28 in		12	10	28	35	1.1	2.8	9.4	49	110
Bens Creek/Blair	≥ 28 in		11	8.0	24	33	0.30	3.2	6.2	31	97
Lit le Eagle/Dorchester	≥ 28 in	X	54	12	22	25	1.1	4.1	15	29	120
Lower War Eagle/Hagy	≥ 28 in		8	19	66	98	1.0	3.5	51	59	300
Glenalum Tunnel/Splashdam	≥ 28 in		17	7.1	20	35	1.3	2.8	5.7	12	120
Gilbert A/Upper Banner	≥ 28 in		24	6.6	12	15	1.6	3.1	4.8	14	59
Gilbert/Lower Banner	≥ 28 in		17	7.8	14	17	1.6	3.8	5.0	16	57
Douglas/Kennedy	≥ 28 in		22	10	15	16	1.6	7.0	10	16	70
Jewell/Raven	≥ 28 in		19	5.8	7.5	6.5	2.0	3.7	5.0	9.2	30
Iaeger/Jawbone	≥ 28 in		17	4.7	7.8	8.0	0.45	2.4	4.0	11	30
Lower Iaeger/Tiller	≥ 28 in		7	6.0	13	20	1.7	2.3	4.7	12	56
Sewell/Lower Seaboard	≥ 28 in	CC	41	5.1	11	15	0.40	2.6	4.2	9.9	56
Welch/Upper Horsepen	≥ 28 in		10	9.1	16	20	2.0	4.2	9.4	16	64
Lit le Raleigh/Middle Horsepen	≥ 28 in		5	6.1	7.0	4.2	2.9	5.0	5.8	7.3	14
Beckley/War Creek	≥ 28 in		18	9.3	19	22	0.25	4.3	13	25	89
Fire Creek/Lower Horsepen	≥ 28 in		14	9.8	14	12	2.2	5.3	12	16	40
Pocahontas No 6	≥ 28 in		9	9.3	13	8.1	1.4	6.3	12	19	25
Pocahontas No 4	≥ 28 in		13	6.6	12	13	1.2	3.5	5.0	16	39
Pocahontas No 3	≥ 28 in	EE	43	5.4	10	14	0.30	2.3	5.2	12	73

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4b. Thick Coal Samples, ≥28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	N	Mercury Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quartile ppm	Maximum ppm
Waynesburg	≥ 28 in	A	56	0.15	0.16	0.074	0.060	0.13	0.15	0.19	0.53
Sewickley	≥ 28 in	B	40	0.099	0.12	0.067	0.021	0.079	0.098	0.15	0.29
Redstone	≥ 28 in	C	56	0.17	0.23	0.18	0.007	0.10	0.18	0 31	0.93
Pittsburgh	≥ 28 in	D	132	0.13	0.17	0.15	0.003	0.082	0.14	0 21	1.0
Lower Bakerstown	≥ 28 in		12	0.18	0.21	0.16	0.080	0.12	0.15	0 23	0.57
Mahoning	≥ 28 in		6	0.30	0.31	0.065	0.26	0.27	0.28	0.31	0.43
Upper Freeport	≥ 28 in	F	215	0.24	0.31	0.20	0.003	0.20	0.28	0 37	1.7
Lower Freeport	≥ 28 in	G	67	0.23	0.33	0.26	0.003	0.20	0.30	0.43	1.6
Upper Kittanning	≥ 28 in	H	32	0.25	0.37	0.30	0.030	0.11	0.35	0 52	1.4
Middle Kittanning	≥ 28 in	I	168	0.16	0.22	0.19	0.003	0.12	0.18	0 27	1.6
Lower Kittanning/No 6 block	≥ 28 in	J	141	0.14	0.23	0.22	0.003	0.10	0.18	0.32	1.6
Clarion	≥ 28 in	K	47	0.14	0.18	0.15	0.022	0.079	0.13	0 24	0.76
Brookville	≥ 28 in	L	30	0.19	0.25	0.26	0.048	0.12	0.21	0 29	1.5
No 5 Block	≥ 28 in	M	65	0.13	0.17	0.12	0.024	0.083	0.14	0 25	0.52
Lower Mercer	≥ 28 in		7	0.24	0.29	0.15	0.040	0.23	0.26	0.40	0.48
Stockton	≥ 28 in	N	51	0.10	0.15	0.14	0.007	0.059	0.11	0.19	0.62
Coalburg	≥ 28 in	O	67	0.089	0.12	0.11	0.007	0.060	0.082	0.16	0.52
Winifrede/Hazard	≥ 28 in	P	48	0.084	0.14	0.18	0.007	0.042	0.078	0.17	1.0
Chilton/Taylor	≥ 28 in		9	0.14	0.17	0.085	0.043	0.12	0.16	0.18	0.30
Fire Clay Rider	≥ 28 in		13	0.16	0.18	0.13	0.083	0.12	0.12	0.18	0.58
Fire Clay	≥ 28 in	Q	40	0.085	0.13	0.10	0.007	0.050	0.087	0.19	0.43
Cedar Grove/Whitesburg	≥ 28 in		16	0.051	0.089	0.086	0.003	0.030	0.050	0.13	0.26
Williamson/Amburgy	≥ 28 in		19	0.081	0.13	0.10	0.010	0.039	0.085	0.22	0.35
Campbell Creek/Upper Elkhorn No 3	≥ 28 in	T	80	0.085	0.12	0.096	0.007	0.055	0.091	0.15	0.52
Upper Elkhorn Nos 1 and 2/Powellton	≥ 28 in	U	59	0.10	0.14	0.13	0.014	0.060	0.095	0.18	0.81
Pond Creek	≥ 28 in	V	78	0.068	0.097	0.090	0.003	0.044	0.070	0.12	0.46
Matewan/Clintwood	≥ 28 in	W	54	0.058	0.10	0.088	0.003	0.035	0.083	0.14	0.36
Middle War Eagle/Eagle	≥ 28 in		12	0.082	0.13	0.12	0.007	0.035	0.14	0.18	0.45
Bens Creek/Blair	≥ 28 in		11	0.045	0.088	0.10	0.007	0.025	0.039	0.11	0.28
Lit le Eagle/Dorchester	≥ 28 in	X	54	0.095	0.13	0.10	0.010	0.055	0.087	0 20	0.40
Lower War Eagle/Hagy	≥ 28 in		8	0.11	0.18	0.11	0.003	0.090	0.20	0.28	0.29
Glenalum Tunnel/Splashdam	≥ 28 in		17	0.12	0.17	0.14	0.045	0.065	0.12	0 25	0.55
Gilbert A/Upper Banner	≥ 28 in		24	0.071	0.11	0.12	0.003	0.050	0.075	0.13	0.51
Gilbert/Lower Banner	≥ 28 in		17	0.046	0.092	0.10	0.003	0.021	0.050	0.082	0.35
Douglas/Kennedy	≥ 28 in		22	0.067	0.11	0.11	0.007	0.050	0.068	0.14	0.50
Jewell/Raven	≥ 28 in		19	0.074	0.10	0.091	0.015	0.050	0.060	0.13	0.37
Iaeger/Jawbone	≥ 28 in		17	0.077	0.12	0.10	0.007	0.050	0.10	0.17	0.41
Lower Iaeger/Tiller	≥ 28 in		7	0.051	0.19	0.36	0.007	0.021	0.052	0.11	1.0
Sewell/Lower Seaboard	≥ 28 in	CC	41	0.12	0.21	0.24	0.017	0.059	0.13	0 25	0.97
Welch/Upper Horsepen	≥ 28 in		10	0.073	0.093	0.075	0.030	0.053	0.069	0.082	0.25
Lit le Raleigh/Middle Horsepen	≥ 28 in		5	0.13	0.14	0.082	0.068	0.082	0.12	0.17	0.27
Beckley/War Creek	≥ 28 in		18	0.067	0.18	0.41	0.007	0.046	0.078	0.11	1.8
Fire Creek/Lower Horsepen	≥ 28 in		14	0.074	0.090	0.058	0.025	0.042	0.070	0.13	0.19
Pocahontas No 6	≥ 28 in		10	0.084	0.21	0.26	0.015	0.022	0.074	0.36	0.66
Pocahontas No 4	≥ 28 in		13	0.042	0.054	0.031	0.007	0.039	0.050	0.080	0.095
Pocahontas No 3	≥ 28 in	EE	43	0.056	0.081	0.079	0.007	0.046	0.065	0.10	0.47

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. thcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4b. Thick Coal Samples, ≥28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	Manganese							
			N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quartile ppm	Maximum ppm
Waynesburg	≥ 28 in	A	56	27	32	28	11	20	25	37	180
Sewickley	≥ 28 in	B	40	18	27	42	6.4	11	15	23	260
Redstone	≥ 28 in	C	56	25	35	31	5.0	17	24	36	140
Pittsburgh	≥ 28 in	D	132	21	29	33	1.4	14	20	36	300
Lower Bakerstown	≥ 28 in		12	18	26	25	6.6	12	15	25	75
Mahoning	≥ 28 in		6	13	16	10	4.9	9.1	14	23	30
Upper Freeport	≥ 28 in	F	215	16	22	20	2.5	10	16	27	140
Lower Freeport	≥ 28 in	G	67	14	31	87	0.92	8.2	13	21	690
Upper Kittanning	≥ 28 in	H	32	14	22	31	3.3	8.3	12	24	170
Middle Kittanning	≥ 28 in	I	167	20	27	32	3.7	12	19	32	310
Lower Kittanning/No 6 block	≥ 28 in	J	141	16	26	48	1.6	9.8	14	26	430
Clarion	≥ 28 in	K	47	20	27	32	3.6	13	21	28	220
Brookville	≥ 28 in	L	30	15	19	12	2.3	10	14	25	52
No 5 Block	≥ 28 in	M	65	8.1	15	27	1.4	4.1	7.5	12	200
Lower Mercer	≥ 28 in		7	11	14	11	4.1	5.6	12	19	35
Stockton	≥ 28 in	N	51	6.8	8.7	5.9	1.2	5.3	6.9	11	25
Coalburg	≥ 28 in	O	67	8.7	11	8.2	1.1	5.7	9.1	13	54
Winifrede/Hazard	≥ 28 in	P	48	11	15	17	1.9	6.2	9.5	16	83
Chilton/Taylor	≥ 28 in		9	12	20	27	3.0	8.8	9.6	13	89
Fire Clay Rider	≥ 28 in		13	16	20	15	3.6	11	15	24	56
Fire Clay	≥ 28 in	Q	40	9.2	14	18	1.9	5.0	8.2	16	86
Cedar Grove/Whitesburg	≥ 28 in		16	13	46	130	2.6	6.0	9.1	19	530
Williamson/Amburgy	≥ 28 in		19	13	27	55	2.8	7.5	11	19	250
Campbell Creek/Upper Elkhorn No 3	≥ 28 in	T	80	9.4	13	12	1.2	5.5	8.8	16	63
Upper Elkhorn Nos 1 and 2/Powellton	≥ 28 in	U	59	8.9	14	17	0.96	4.6	9.2	17	110
Pond Creek	≥ 28 in	V	78	13	29	67	2.2	6.6	12	23	540
Matewan/Clintwood	≥ 28 in	W	54	7.9	14	23	1.1	3.9	7.3	14	150
Middle War Eagle/Eagle	≥ 28 in		12	9.0	21	32	1.7	3.7	7.7	16	100
Bens Creek/Blair	≥ 28 in		11	7.0	15	24	3.0	3.8	4.9	5.7	68
Lit le Eagle/Dorchester	≥ 28 in	X	54	10	21	35	1.1	4.7	8.9	16	170
Lower War Eagle/Hagy	≥ 28 in		8	13	27	39	2.4	5.6	17	25	120
Glenalum Tunnel/Splashdam	≥ 28 in		17	12	20	23	2.1	4.6	11	29	84
Gilbert A/Upper Banner	≥ 28 in		24	13	17	12	3.9	7.3	15	22	53
Gilbert/Lower Banner	≥ 28 in		17	23	29	18	4.5	16	23	50	60
Douglas/Kennedy	≥ 28 in		22	20	35	45	2.9	11	24	32	190
Jewell/Raven	≥ 28 in		19	24	29	18	7.8	16	23	36	74
Iaeger/Jawbone	≥ 28 in		17	18	35	43	1.2	8.7	15	37	160
Lower Iaeger/Tiller	≥ 28 in		7	21	24	13	10	16	17	33	45
Sewell/Lower Seaboard	≥ 28 in	CC	41	9.3	17	21	1.5	4.4	8.2	21	100
Welch/Upper Horsepen	≥ 28 in		10	10	12	7.3	5.2	6.4	9.7	16	27
Lit le Raleigh/Middle Horsepen	≥ 28 in		4	39	91	130	8.3	16	38	110	280
Beckley/War Creek	≥ 28 in		18	9.6	30	70	1.4	4.8	6.3	22	300
Fire Creek/Lower Horsepen	≥ 28 in		14	6.6	8.1	5.1	2.7	3.5	7.5	12	19
Pocahontas No 6	≥ 28 in		10	8.4	22	42	1.5	2.8	11	15	140
Pocahontas No 4	≥ 28 in		13	18	37	68	3.4	8.5	21	30	260
Pocahontas No 3	≥ 28 in	EE	43	17	25	31	1.7	9.4	20	27	200

Table 4. Coal quality statistics for coal beds with > 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese:
a. all, b. hcik (> 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N > 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4c. Thin Coal Smples, <28 inch thick.

| | | | | Selenium | | | | | | | |
Coal bed name, this study	Thickness range	Coal bed code N≥30	N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quar ile ppm	Maximum ppm
Redstone	< 28 in		18	2.3	2.6	1.5	1.1	1.7	2.3	3.0	7.0
Pittsburgh Roof	< 28 in		8	2.1	2.3	1.1	1.4	1.5	1.8	2.7	4.4
Pittsburgh	< 28 in		5	1.5	1.7	1.0	0.70	1.3	1.4	1.5	3.4
Harlem	< 28 in		8	1.1	1.2	0.32	0.68	0.95	1.3	1.4	1.6
Lower Bakerstown	< 28 in		18	2.9	3.3	2.2	1.5	2.1	2.8	3.8	11
Brush Creek	< 28 in		8	2.7	3.1	1.7	1.2	2.0	2.6	3.6	6.4
Mahoning	< 28 in		14	1.8	2.0	0.91	1.2	1.4	1.6	2.3	4.7
Upper Freeport	< 28 in	F	62	2.6	3.2	2.6	0.43	1.8	2.3	3.7	14
Lower Freeport	< 28 in	G	36	3.0	3.4	1.8	0.90	2.2	3.3	4.3	9.1
Upper Kittanning	< 28 in	H	35	3.3	3.9	2.6	1.3	2.3	2.9	4.7	11
Middle Kittanning Rider	< 28 in		8	4.5	5.2	2.3	1.0	3.6	5.9	6.6	8.1
Middle Kittanning	< 28 in	I	75	3.1	3.6	2.3	0.99	2.4	3.0	3.9	14
Strasburg	< 28 in		10	3.8	4.1	1.5	1.5	3.7	4.0	4.1	7.7
Lower Kittanning Rider	< 28 in		6	2.9	3.1	1.2	1.6	2.3	2.9	3.8	4.8
Lower Kittanning/No 6 block	< 28 in	J	57	3.4	4.1	2.7	0.98	2.3	3.2	4.5	14
Clarion	< 28 in		27	4.9	5.6	2.5	1.2	3.3	5.4	8.0	9.5
Brookville	< 28 in	L	43	4.6	5.4	3.6	1.2	3.3	4.4	6.4	21
No 5 Block	< 28 in		28	4.7	6.4	4.0	0.10	3.6	5.9	8.5	18
Upper Mercer	< 28 in		6	6.3	6.8	3.0	3.1	5.5	6.6	7.2	12
Lower Mercer	< 28 in		17	5.6	6.6	3.0	0.84	5.6	6.5	8.2	13
Quakertown	< 28 in		7	5.5	6.9	4.2	1.2	4.1	5.7	11	12
Stockton	< 28 in		11	4.8	5.2	2.2	2.4	3.9	4.6	6.3	8.7
Coalburg	< 28 in	O	76	4.4	4.9	2.2	1.2	3.3	4.7	5.7	12
Winifrede/Hazard	< 28 in	P	31	4.0	4.5	2.0	0.50	3.2	3.9	5.8	9.2
Lower Winifrede/Hazard	< 28 in		6	2.2	3.7	1.9	0.07	3.8	4.0	4.3	5.9
Chilton/Taylor	< 28 in		6	4.2	4.8	2.7	2.0	3.2	3.6	6.6	8.7
Fire Clay Rider	< 28 in		16	4.1	4.9	3.3	1.7	2.7	4.1	4.9	13
Fire Clay	< 28 in	Q	30	3.8	4.2	2.0	1.7	2.6	3.8	5.5	9.0
Cedar Grove/Whitesburg	< 28 in		23	4.0	4.4	2.1	1.2	2.8	4.3	5.1	9.4
Williamson/Amburgy	< 28 in		26	2.9	3.2	1.6	1.0	2.1	2.8	4.3	7.4
Campbell Creek/Upper Elkhorn No 3	< 28 in	T	63	2.9	3.5	2.0	0.07	2.0	2.9	4.3	9.3
Upper Elkhorn Nos 1 and 2/Powellton	< 28 in	U	55	2.7	3.2	2.5	0.64	1.9	2.6	3.4	16
Pond Creek	< 28 in	V	43	2.7	2.9	1.2	1.2	2.1	3.0	3.4	6.6
Matewan/Clintwood	< 28 in	W	72	2.2	2.6	1.6	0.62	1.5	2.2	3.0	8.0
Middle War Eagle/Eagle	< 28 in		11	2.7	3.4	2.7	1.1	2.0	2.4	3.5	9.3
Lit le Eagle/Dorchester	< 28 in	X	34	1.9	2.2	1.3	0.63	1.4	1.8	2.7	7.0
Lower War Eagle/Hagy	< 28 in		5	3.1	3.1	0.65	2.0	3.2	3.3	3.5	3.6
Glenalum Tunnel/Splashdam	< 28 in		18	2.2	2.3	0.66	1.4	1.7	2.3	2.8	3.8
Gilbert A/Upper Banner	< 28 in		22	2.4	2.7	1.4	1.2	1.6	2.3	3.3	6.7
Gilbert/Lower Banner	< 28 in		6	2.8	3.0	1.2	1.4	2.3	2.8	3.9	4.7
Douglas/Kennedy	< 28 in		15	2.0	2.2	1.1	0.90	1.5	1.8	2.7	4.6
Jewell/Raven	< 28 in		5	2.4	2.9	2.0	0.88	1.7	2.4	3.7	5.9
Iaeger/Jawbone	< 28 in		17	2.3	2.9	2.4	0.70	1.7	2.5	3.2	11
Lower Iaeger/Tiller	< 28 in		10	2.4	2.6	1.1	1.5	2.0	2.4	2.8	5.4
Sewell/Lower Seaboard	< 28 in		20	2.1	2.7	2.1	0.79	1.1	1.9	4.1	7.0
Welch/Upper Horsepen	< 28 in		5	1.8	1.9	0.56	1.0	1.8	1.8	2.2	2.5
Beckley/War Creek	< 28 in		12	1.8	2.2	1.8	0.80	1.2	1.6	2.3	7.0
Fire Creek/Lower Horsepen	< 28 in		8	1.5	1.8	1.1	0.67	0.96	1.9	2.0	4.0
Pocahontas No 7	< 28 in		4	1.7	2.0	1.4	1.0	1.2	1.6	2.4	4.0
Pocahontas No 3	< 28 in		10	3.1	3.5	1.7	1.9	2.1	2.6	5.2	6.0

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. hcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4c. Thin Coal Smples, <28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	Thickness							
			N	Geometric mean in	Average in	Standard Deviation in	Minimum in	Lower Quartile in	Median in	Upper Quar ile in	Maximum in
Redstone	< 28 in		18	19.0	19.3	3.5	12.0	17.0	18.0	21.6	25.3
Pittsburgh Roof	< 28 in		8	20.3	21.1	5.8	10.2	18.4	23.2	24.2	27.6
Pittsburgh	< 28 in		5	20.6	22.1	7.5	9.0	23.8	24.5	25.8	27.5
Harlem	< 28 in		8	23.0	23.3	4.0	17.5	19.6	25.4	26.3	27.0
Lower Bakerstown	< 28 in		18	22.8	23.2	4.1	13.2	20.9	24.3	26.4	27.6
Brush Creek	< 28 in		8	14.5	15.6	5.8	7.8	12.9	14.7	20.0	24.6
Mahoning	< 28 in		14	17.6	18.8	5.7	4.8	16.1	19.1	22.4	27.0
Upper Freeport	< 28 in	F	63	16.6	18.3	6.6	2.0	13.0	19.0	24.0	27.0
Lower Freeport	< 28 in	G	36	18.1	19.3	6.3	5.4	14.9	19.5	25.6	27.6
Upper Kittanning	< 28 in	H	35	18.3	19.3	5.6	6.6	15.3	20.4	23.7	27.6
Middle Kittanning Rider	< 28 in		8	12.6	15.2	8.3	3.0	11.4	15.0	19.5	27.6
Middle Kittanning	< 28 in	I	75	18.7	20.1	6.1	2.5	16.7	21.3	25.2	27.8
Strasburg	< 28 in		10	17.8	18.5	5.5	12.8	14.1	16.3	22.2	27.9
Lower Kittanning Rider	< 28 in		6	11.0	11.6	4.2	6.6	9.8	11.1	12.0	19.2
Lower Kittanning/No 6 block	< 28 in	J	57	21.6	22.1	4.3	9.8	20.4	23.0	25.2	27.8
Clarion	< 28 in		27	16.7	17.6	5.4	9.0	13.8	18.0	20.6	26.4
Brookville	< 28 in	L	43	17.3	18.0	4.9	6.6	15.6	18.3	21.2	27.6
No 5 Block	< 28 in		28	16.4	17.5	5.9	7.4	12.8	17.8	21.7	27.6
Upper Mercer	< 28 in		6	17.8	18.6	5.9	11.4	14.1	18.3	23.0	26.4
Lower Mercer	< 28 in		17	20.4	21.1	5.2	10.8	18.0	24.0	24.6	27.0
Quakertown	< 28 in		7	22.0	22.2	2.8	18.5	19.8	22.8	24.3	26.0
Stockton	< 28 in		11	11.3	12.3	5.3	5.9	7.9	12.5	15.2	23.6
Coalburg	< 28 in	O	76	16.1	17.3	5.9	4.3	13.3	18.0	21.1	27.8
Winifrede/Hazard	< 28 in	P	31	15.6	17.0	6.4	4.3	11.4	19.0	22.0	26.8
Lower Winifrede/Hazard	< 28 in		6	15.9	17.3	6.8	6.7	14.2	17.8	21.3	26.0
Chilton/Taylor	< 28 in		6	10.5	12.0	6.9	5.5	6.6	10.9	15.0	23.5
Fire Clay Rider	< 28 in		16	12.4	14.4	7.8	6.0	7.6	13.2	18.8	27.2
Fire Clay	< 28 in	Q	30	16.1	17.5	6.6	6.0	12.2	18.5	22.6	27.6
Cedar Grove/Whitesburg	< 28 in		23	14.5	16.5	7.2	3.1	11.7	16.1	22.6	26.8
Williamson/Amburgy	< 28 in		26	15.0	16.1	6.0	5.5	11.2	15.4	21.1	27.2
Campbell Creek/Upper Elkhorn No 3	< 28 in	T	63	18.0	19.0	5.8	7.0	15.2	20.0	23.2	27.6
Upper Elkhorn Nos 1 and 2/Powellton	< 28 in	U	55	15.1	16.2	5.7	7.1	12.3	15.4	20.7	27.2
Pond Creek	< 28 in	V	43	17.1	18.8	6.7	4.0	13.9	20.0	24.2	27.8
Matewan/Clintwood	< 28 in	W	72	16.9	17.8	5.6	7.7	13.2	18.0	22.8	27.6
Middle War Eagle/Eagle	< 28 in		11	19.0	19.5	4.8	12.6	16.7	18.5	22.6	28.0
Lit le Eagle/Dorchester	< 28 in	X	34	18.9	19.7	5.2	10.2	17.0	20.8	23.9	27.0
Lower War Eagle/Hagy	< 28 in		5	17.4	19.6	8.2	6.0	19.2	22.2	22.8	27.6
Glenalum Tunnel/Splashdam	< 28 in		18	18.6	19.4	5.8	11.0	14.9	17.3	25.4	27.6
Gilbert A/Upper Banner	< 28 in		22	15.8	17.2	6.6	6.3	12.3	17.0	23.5	27.0
Gilbert/Lower Banner	< 28 in		6	18.7	19.3	4.9	12.8	15.6	19.9	22.4	25.8
Douglas/Kennedy	< 28 in		15	23.9	24.1	3.1	18.0	22.0	24.0	27.0	27.6
Jewell/Raven	< 28 in		5	11.2	12.5	6.4	6.0	7.5	10.8	17.0	21.0
Iaeger/Jawbone	< 28 in		17	19.1	20.6	7.1	8.4	15.1	24.5	26.6	27.6
Lower Iaeger/Tiller	< 28 in		10	10.7	11.6	5.1	5.4	8.3	10.5	13.2	21.6
Sewell/Lower Seaboard	< 28 in		20	19.7	20.1	4.0	12.5	18.0	20.5	23.5	25.5
Welch/Upper Horsepen	< 28 in		5	17.8	18.6	5.7	11.0	16.0	18.0	22.0	26.0
Beckley/War Creek	< 28 in		12	17.3	18.7	7.0	8.0	12.8	19.0	24.5	27.8
Fire Creek/Lower Horsepen	< 28 in		8	19.5	19.9	4.3	14.0	17.8	19.0	21.3	26.9
Pocahontas No 7	< 28 in		5	15.8	16.3	4.6	10.5	14.0	17.0	17.2	23.0
Pocahontas No 3	< 28 in		10	18.3	19.2	6.0	11.1	13.3	20.8	24.3	27.0

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese:
a. all, b. hcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4c. Thin Coal Smples, <28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	N	Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quarile percent	Maximum percent
								Ash Yield			
Redstone	< 28 in		18	12.50	13.18	4.97	9.10	10.08	10.95	14.09	27.20
Pittsburgh Roof	< 28 in		8	15.94	16.29	3.65	11.90	13.25	16.22	18.04	22.30
Pittsburgh	< 28 in		5	10.55	10.72	2.24	8.30	10.20	10.20	10.49	14.40
Harlem	< 28 in		8	10.12	10.34	2.20	7.30	9.19	10.25	11.95	13.02
Lower Bakerstown	< 28 in		18	11.25	12.42	6.22	5.66	8.98	10.39	14.04	29.30
Brush Creek	< 28 in		8	11.64	12.55	5.78	7.17	8.78	11.28	13.76	25.50
Mahoning	< 28 in		13	11.02	11.63	4.30	7.00	8.90	9.77	13.05	20.23
Upper Freeport	< 28 in	F	49	12.11	13.37	6.03	5.50	8.20	12.10	16.36	29.31
Lower Freeport	< 28 in	G	36	13.71	14.72	6.09	8.43	9.71	12.02	17.79	31.20
Upper Kittanning	< 28 in	H	35	13.43	14.27	4.92	4.54	11.72	13.44	17.18	30.21
Middle Kittanning Rider	< 28 in		8	9.03	10.13	5.68	4.50	7.50	8.80	10.65	22.70
Middle Kittanning	< 28 in	I	74	9.47	10.98	5.91	1.70	7.04	10.21	13.58	28.66
Strasburg	< 28 in		10	11.33	11.78	3.31	6.30	9.35	11.90	13.65	16.80
Lower Kittanning Rider	< 28 in		6	11.20	13.12	8.22	5.70	6.80	11.78	15.59	27.44
Lower Kittanning/No 6 block	< 28 in	J	55	11.30	12.14	4.70	5.00	8.79	11.07	14.15	23.70
Clarion	< 28 in		27	12.28	13.55	5.55	4.20	8.80	14.70	17.04	25.57
Brookville	< 28 in	L	43	12.14	13.24	5.51	5.30	8.75	13.30	16.75	27.75
No 5 Block	< 28 in		27	11.42	12.94	6.94	4.20	7.65	11.58	15.39	31.50
Upper Mercer	< 28 in		6	18.82	18.99	2.72	15.22	17.47	19.08	20.18	23.07
Lower Mercer	< 28 in		16	15.31	16.40	5.41	4.80	13.54	16.76	20.85	24.34
Quakertown	< 28 in		7	10.50	11.60	4.44	3.30	10.11	12.81	13.81	17.23
Stockton	< 28 in		11	12.19	12.97	5.79	8.11	10.72	11.80	12.99	29.60
Coalburg	< 28 in	O	75	8.23	9.56	5.43	2.70	5.79	8.78	12.35	29.10
Winifrede/Hazard	< 28 in	P	31	7.74	9.90	6.85	2.00	3.61	9.30	13.30	26.40
Lower Winifrede/Hazard	< 28 in		6	7.98	8.99	4.43	3.50	5.70	9.06	11.73	15.10
Chilton/Taylor	< 28 in		6	12.13	14.09	8.76	5.70	8.32	12.58	15.75	30.00
Fire Clay Rider	< 28 in		10	11.13	13.72	9.57	3.65	7.99	10.42	16.31	32.90
Fire Clay	< 28 in	Q *	26	8.96	10.52	5.94	2.50	6.21	10.75	12.88	24.80
Cedar Grove/Whitesburg	< 28 in		22	9.33	10.09	3.86	3.32	7.63	9.83	12.83	18.09
Williamson/Amburgy	< 28 in		25	7.63	8.64	4.73	2.76	5.94	7.80	10.64	24.40
Campbell Creek/Upper Elkhorn No 3	< 28 in	T	63	5.54	6.92	4.36	0.90	3.41	5.40	9.44	19.10
Upper Elkhorn Nos 1 and 2/Powellton	< 28 in	U	52	5.54	6.62	4.32	1.60	4.24	5.85	8.09	22.37
Pond Creek	< 28 in	V	43	5.11	6.31	4.14	1.22	3.29	5.00	8.80	16.40
Matewan/Clintwood	< 28 in	W	71	5.96	6.85	3.63	1.73	3.85	6.00	9.01	19.70
Middle War Eagle/Eagle	< 28 in		11	5.46	6.18	3.23	1.66	4.19	6.30	6.55	14.01
Lit le Eagle/Dorchester	< 28 in	X	34	5.69	6.84	4.20	2.20	3.73	5.60	10.19	17.00
Lower War Eagle/Hagy	< 28 in		4	9.53	10.05	3.53	5.66	8.14	10.39	12.30	13.78
Glenalum Tunnel/Splashdam	< 28 in		18	4.11	5.05	4.07	1.74	2.53	4.11	6.05	19.10
Gilbert A/Upper Banner	< 28 in		19	8.01	8.90	4.41	3.65	6.10	7.05	11.46	20.67
Gilbert/Lower Banner	< 28 in		6	5.88	6.35	2.79	3.40	4.57	6.28	6.69	11.30
Douglas/Kennedy	< 28 in		14	6.22	8.03	7.46	2.75	4.38	4.69	7.80	29.55
Jewell/Raven	< 28 in		3	7.70	8.71	5.55	5.13	na	5.90	na	15.10
Iaeger/Jawbone	< 28 in		17	7.65	10.34	7.61	2.00	3.80	9.80	15.40	29.30
Lower Iaeger/Tiller	< 28 in		10	9.02	10.35	5.27	2.90	7.40	9.70	12.88	19.40
Sewell/Lower Seaboard	< 28 in		15	10.69	11.90	5.34	3.10	9.00	11.49	13.40	21.60
Welch/Upper Horsepen	< 28 in		2	7.28	7.32	0.97	6.63	na	na	na	8.00
Beckley/War Creek	< 28 in		11	6.85	9.13	8.00	2.00	4.25	7.30	10.15	29.30
Fire Creek/Lower Horsepen	< 28 in		8	5.19	5.82	2.74	2.60	3.07	6.34	7.65	10.00
Pocahontas No 7	< 28 in		5	11.09	13.48	9.72	4.81	8.32	8.92	16.10	29.25
Pocahontas No 3	< 28 in		8	7.97	9.49	7.07	3.80	6.23	7.15	10.08	26.00

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese:
a. all, b. hcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4c. Thin Coal Smples, <28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	N	Sulfur Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quar ile percent	Maximum percent
Redstone	< 28 in		18	2.81	3.08	1.22	0.80	2.24	3.19	3.55	5.90
Pittsburgh Roof	< 28 in		8	2.52	3.22	2.08	0.60	1.58	3.10	4.71	6.50
Pittsburgh	< 28 in		5	3.26	3.35	0.91	2.56	2.60	3.40	3.40	4.80
Harlem	< 28 in		8	1.40	1.75	1.18	0.50	0.78	1.38	2.75	3.66
Lower Bakerstown	< 28 in		18	2.61	2.92	1.23	0.77	2.39	3.00	3.63	5.41
Brush Creek	< 28 in		8	2.59	2.73	1.04	1.84	2.08	2.32	3.01	5.00
Mahoning	< 28 in		13	2.04	2.31	1.25	0.90	1.43	1.84	3.22	5.10
Upper Freeport	< 28 in	F	60	2.36	2.80	1.73	0.80	1.44	2.44	3.56	8.00
Lower Freeport	< 28 in	G	36	2.81	3.30	1.73	0.60	1.97	3.03	4.53	7.22
Upper Kittanning	< 28 in	H	35	1.53	1.90	1.25	0.47	0.87	1.59	2.78	5.72
Middle Kittanning Rider	< 28 in		8	1.25	1.79	1.47	0.50	0.50	1.55	2.63	4.40
Middle Kittanning	< 28 in	I	74	2.17	2.62	1.65	0.50	1.42	2.06	3.49	8.11
Strasburg	< 28 in		10	4.17	4.81	2.07	1.10	4.25	5.31	6.22	7.20
Lower Kittanning Rider	< 28 in		6	1.25	1.41	0.85	0.82	0.90	0.96	1.68	2.93
Lower Kittanning/No 6 block	< 28 in	J	55	3.08	3.59	1.91	0.43	2.39	3.30	4.79	10.40
Clarion	< 28 in		27	2.77	3.24	1.52	0.50	2.30	3.30	3.95	6.40
Brookville	< 28 in	L	43	2.25	2.62	1.57	0.70	1.67	2.40	2.92	7.85
No 5 Block	< 28 in		27	1.34	1.65	1.11	0.50	0.80	1.02	2.15	4.30
Upper Mercer	< 28 in		6	3.82	4.02	1.35	2.19	3.18	4.07	4.72	5.96
Lower Mercer	< 28 in		16	2.03	2.45	1.37	0.51	1.49	1.99	3.74	4.69
Quakertown	< 28 in		7	1.99	2.70	2.37	0.80	1.09	1.71	3.49	7.21
Stockton	< 28 in		11	1.53	2.06	1.64	0.50	0.75	1.60	3.26	5.50
Coalburg	< 28 in	O	75	1.19	1.46	1.05	0.50	0.73	1.00	1.90	4.70
Winifrede/Hazard	< 28 in	P	31	0.96	1.15	0.89	0.41	0.67	0.80	1.27	4.70
Lower Winifrede/Hazard	< 28 in		6	0.77	0.80	0.26	0.60	0.68	0.70	0.81	1.30
Chilton/Taylor	< 28 in		6	2.03	2.54	1.60	0.70	1.25	2.77	3.21	4.90
Fire Clay Rider	< 28 in		10	2.29	2.79	1.68	0.80	1.30	2.70	3.93	5.20
Fire Clay	< 28 in	Q *	26	1.10	1.43	1.31	0.56	0.68	0.81	1.36	5.95
Cedar Grove/Whitesburg	< 28 in		22	1.73	2.09	1.25	0.70	0.93	1.88	3.06	4.30
Williamson/Amburgy	< 28 in		25	1.66	2.02	1.38	0.60	0.90	1.71	2.40	5.80
Campbell Creek/Upper Elkhorn No 3	< 28 in	T	63	1.16	1.44	1.09	0.50	0.70	0.90	1.87	5.10
Upper Elkhorn Nos 1 and 2/Powellton	< 28 in	U	52	1.56	2.02	1.53	0.50	0.82	1.31	2.78	6.60
Pond Creek	< 28 in	V	43	1.43	1.84	1.38	0.50	0.80	1.20	2.59	6.30
Matewan/Clintwood	< 28 in	W	71	1.42	1.85	1.47	0.54	0.80	1.12	2.60	6.61
Middle War Eagle/Eagle	< 28 in		11	1.55	1.76	0.90	0.60	1.08	1.50	2.62	3.10
Lit le Eagle/Dorchester	< 28 in	X	34	1.15	1.37	1.05	0.50	0.88	1.00	1.35	5.00
Lower War Eagle/Hagy	< 28 in		4	1.99	2.25	1.21	1.20	1.23	2.09	3.11	3.60
Glenalum Tunnel/Splashdam	< 28 in		18	1.01	1.30	1.19	0.60	0.64	0.70	1.49	5.20
Gilbert A/Upper Banner	< 28 in		19	1.13	1.43	1.24	0.50	0.66	1.08	1.60	5.80
Gilbert/Lower Banner	< 28 in		6	1.10	1.22	0.60	0.60	0.78	1.11	1.50	2.19
Douglas/Kennedy	< 28 in		14	1.09	1.24	0.74	0.68	0.80	0.85	1.42	2.93
Jewell/Raven	< 28 in		3	1.54	1.96	1.69	0.80	na	1.17	na	3.90
Iaeger/Jawbone	< 28 in		17	1.14	1.60	1.46	0.50	0.60	0.80	2.00	4.90
Lower Iaeger/Tiller	< 28 in		10	2.33	3.44	2.71	0.60	0.85	3.65	4.43	8.90
Sewell/Lower Seaboard	< 28 in		15	0.86	1.03	0.69	0.40	0.55	0.80	1.21	2.58
Welch/Upper Horsepen	< 28 in		2	0.97	1.02	0.42	0.72	na	na	na	1.31
Beckley/War Creek	< 28 in		11	0.76	0.91	0.78	0.40	0.55	0.70	0.80	3.20
Fire Creek/Lower Horsepen	< 28 in		8	0.81	0.84	0.23	0.57	0.68	0.83	0.95	1.20
Pocahontas No 7	< 28 in		5	0.89	0.95	0.36	0.56	0.56	1.12	1.23	1.27
Pocahontas No 3	< 28 in		8	0.71	0.83	0.55	0.40	0.50	0.60	0.85	1.80

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. hcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4c. Thin Coal Smples, <28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	N	Geometric mean percent	Average percent	Standard Deviation percent	Minimum percent	Lower Quartile percent	Median percent	Upper Quar ile percent	Maximum percent
							Pyritic Sulfur				
Redstone	< 28 in		16	1.49	1.82	0.99	0.19	1.12	1.79	2.37	3.51
Pittsburgh Roof	< 28 in		8	1.09	2.26	1.96	0.03	0.82	2.09	3.38	5.74
Pittsburgh	< 28 in		5	2.15	2.24	0.73	1.45	1.84	2.02	2.55	3.33
Harlem	< 28 in		8	0.60	0.98	0.85	0.07	0.25	0.89	1.38	2.44
Lower Bakerstown	< 28 in		18	1.33	1.76	0.92	0.09	1.24	1.86	2.39	3.46
Brush Creek	< 28 in		8	1.70	1.86	0.99	1.12	1.38	1.49	1.94	4.17
Mahoning	< 28 in		12	1.01	1.40	0.98	0.08	0.70	1.24	2.08	3.34
Upper Freeport	< 28 in	F	56	1.36	1.80	1.37	0.14	0.76	1.47	2.43	6.18
Lower Freeport	< 28 in	G	36	1.58	2.12	1.26	0.05	1.15	1.88	3.03	5.43
Upper Kittanning	< 28 in	H	34	0.58	1.25	1.13	0.01	0.28	1.00	2.12	4.21
Middle Kittanning Rider	< 28 in		8	0.30	1.06	1.10	0.02	0.04	0.99	1.73	2.89
Middle Kittanning	< 28 in	I	73	1.07	1.75	1.47	0.01	0.94	1.28	2.52	6.85
Strasburg	< 28 in		10	2.48	3.13	1.63	0.38	2.71	3.29	4.18	5.48
Lower Kittanning Rider	< 28 in		6	0.31	0.53	0.64	0.07	0.16	0.33	0.51	1.78
Lower Kittanning/No 6 block	< 28 in	J	52	1.83	2.38	1.46	0.02	1.40	2.08	3.13	8.08
Clarion	< 28 in		27	1.31	2.08	1.26	0.03	1.58	1.97	2.89	4.73
Brookville	< 28 in	L	42	1.04	1.45	1.30	0.07	0.60	1.14	1.78	7.10
No 5 Block	< 28 in		24	0.51	1.10	1.08	0.01	0.26	0.72	1.63	3.46
Upper Mercer	< 28 in		6	2.96	3.22	1.28	1.31	2.53	3.29	4.19	4.66
Lower Mercer	< 28 in		16	0.94	1.66	1.23	0.02	0.83	1.26	2.62	3.69
Quakertown	< 28 in		7	1.19	2.14	2.37	0.15	0.76	1.19	2.66	6.81
Stockton	< 28 in		8	0.43	1.43	1.71	0.04	0.08	1.02	2.18	4.85
Coalburg	< 28 in	O	69	0.32	0.76	0.95	0.01	0.10	0.29	1.05	3.99
Winifrede/Hazard	< 28 in	P *	29	0.18	0.50	0.80	0.01	0.08	0.15	0.74	3.66
Lower Winifrede/Hazard	< 28 in		6	0.13	0.22	0.29	0.04	0.07	0.12	0.15	0.80
Chilton/Taylor	< 28 in		5	1.21	1.99	1.11	0.07	2.24	2.25	2.55	2.86
Fire Clay Rider	< 28 in		10	1.07	1.87	1.56	0.06	0.61	1.49	2.94	4.21
Fire Clay	< 28 in	Q *	26	0.25	0.63	0.88	0.02	0.09	0.26	0.62	3.33
Cedar Grove/Whitesburg	< 28 in		16	1.17	1.62	1.03	0.09	0.91	1.54	2.41	3.54
Williamson/Amburgy	< 28 in		23	0.57	1.07	1.01	0.02	0.34	0.70	1.54	4.18
Campbell Creek/Upper Elkhorn No 3	< 28 in	T	37	0.31	0.85	1.05	0.03	0.09	0.25	1.41	3.50
Upper Elkhorn Nos 1 and 2/Powellton	< 28 in	U	48	0.52	1.28	1.36	0.01	0.19	0.88	1.86	5.17
Pond Creek	< 28 in	V	33	0.41	1.10	1.12	0.02	0.10	0.62	1.88	3.78
Matewan/Clintwood	< 28 in	W	70	0.42	1.04	1.22	0.01	0.15	0.42	1.85	5.22
Middle War Eagle/Eagle	< 28 in		10	0.68	0.98	0.72	0.06	0.54	0.74	1.62	2.06
Lit le Eagle/Dorchester	< 28 in	X	34	0.33	0.59	0.74	0.03	0.19	0.31	0.55	3.27
Lower War Eagle/Hagy	< 28 in		4	0.94	1.42	1.22	0.23	0.49	1.33	2.25	2.80
Glenalum Tunnel/Splashdam	< 28 in		18	0.19	0.66	1.01	0.01	0.06	0.17	0.82	3.65
Gilbert A/Upper Banner	< 28 in		19	0.27	0.77	1.31	0.01	0.10	0.43	0.71	5.72
Gilbert/Lower Banner	< 28 in		5	0.37	0.57	0.50	0.06	0.30	0.40	0.71	1.36
Douglas/Kennedy	< 28 in		12	0.29	0.52	0.62	0.05	0.15	0.27	0.54	2.07
Jewell/Raven	< 28 in		3	0.52	1.34	1.97	0.18	na	0.22	na	3.61
Iaeger/Jawbone	< 28 in		15	0.28	0.94	1.18	0.03	0.07	0.17	1.71	3.23
Lower Iaeger/Tiller	< 28 in		10	1.30	2.74	2.45	0.08	0.55	2.83	4.10	7.62
Sewell/Lower Seaboard	< 28 in		12	0.38	0.60	0.53	0.05	0.27	0.42	0.80	1.79
Welch/Upper Horsepen	< 28 in		2	0.07	0.24	0.32	0.01	na	na	na	0.46
Beckley/War Creek	< 28 in		9	0.15	0.36	0.67	0.03	0.10	0.13	0.22	2.14
Fire Creek/Lower Horsepen	< 28 in		6	0.14	0.21	0.17	0.02	0.15	0.17	0.21	0.52
Pocahontas No 7	< 28 in		5	0.14	0.28	0.25	0.02	0.03	0.32	0.39	0.62
Pocahontas No 3	< 28 in		1	na	na	na	na	na	0.22	na	na

Table 4. Coal quality statistics for coal beds with > 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese:
a. all, b. hcik (> 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N > 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4c. Thin Coal Smples, <28 inch thick.

| | | | | | Arsenic | | | | | |
Coal Bed Name This Study	Thickness range	Coal bed code N≥30	N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quar ile ppm	Maximum ppm
Redstone	< 28 in		18	21	44	68	1.5	9.5	20	45	290
Pittsburgh Roof	< 28 in		7	12	17	13	0.85	12	14	22	41
Pittsburgh	< 28 in		5	24	34	27	5.8	13	32	44	75
Harlem	< 28 in		8	7.8	14	17	1.5	4.8	9.3	14	53
Lower Bakerstown	< 28 in		18	39	60	86	9.9	23	43	53	390
Brush Creek	< 28 in		8	28	36	24	10	18	30	50	77
Mahoning	< 28 in		14	79	100	99	28	49	73	120	410
Upper Freeport	< 28 in	F	63	38	51	41	4.3	24	42	66	200
Lower Freeport	< 28 in	G	35	30	45	34	2.3	21	35	75	120
Upper Kittanning	< 28 in	H	35	26	47	49	1.0	10	35	67	230
Middle Kittanning Rider	< 28 in		8	22	43	39	1.4	16	38	61	120
Middle Kittanning	< 28 in	I	72	17	34	38	0.70	7.2	21	43	160
Strasburg	< 28 in		10	18	31	31	2.9	8.1	24	35	100
Lower Kittanning Rider	< 28 in		6	9.5	14	13	3.0	5.5	7.8	18	38
Lower Kittanning/No 6 block	< 28 in	J	57	24	42	52	2.0	11	21	48	270
Clarion	< 28 in		27	12	20	18	1.4	4.2	18	27	73
Brookville	< 28 in	L	43	11	21	29	0.49	4.7	12	20	150
No 5 Block	< 28 in		27	11	28	39	0.90	3.7	12	38	150
Upper Mercer	< 28 in		6	33	44	43	16	20	30	40	130
Lower Mercer	< 28 in		17	13	26	40	1.6	6.4	12	29	160
Quakertown	< 28 in		7	20	28	27	9.5	12	13	36	81
Stockton	< 28 in		11	9.2	20	22	0.70	3.6	7.3	29	61
Coalburg	< 28 in	O	75	8.0	18	28	0.40	3.0	6.6	19	170
Winifrede/Hazard	< 28 in	P	31	5.1	22	59	0.50	1.6	5.0	9.8	270
Lower Winifrede/Hazard	< 28 in		5	6.0	8.1	6.5	2.5	2.6	5.6	13	17
Chilton/Taylor	< 28 in		6	11	25	26	1.2	3.4	17	47	58
Fire Clay Rider	< 28 in		16	35	65	77	1.7	22	38	75	300
Fire Clay	< 28 in	Q	30	7.2	17	23	0.90	2.3	6.2	27	100
Cedar Grove/Whitesburg	< 28 in		23	15	33	57	1.8	5.8	17	38	280
Williamson/Amburgy	< 28 in		26	16	32	36	0.61	8.6	27	36	170
Campbell Creek/Upper Elkhorn No 3	< 28 in	T	62	7.7	21	33	0.90	2.3	5.7	30	170
Upper Elkhorn Nos 1 and 2/Powellton	< 28 in	U	55	23	70	120	1.1	9.5	23	53	680
Pond Creek	< 28 in	V	43	14	32	34	0.40	5.4	15	53	120
Matewan/Clintwood	< 28 in	W	72	11	30	40	0.50	3.6	12	40	180
Middle War Eagle/Eagle	< 28 in		11	28	48	39	1.9	14	34	84	100
Lit le Eagle/Dorchester	< 28 in	X	34	11	24	32	1.1	3.9	13	32	130
Lower War Eagle/Hagy	< 28 in		5	32	89	140	3.5	13	48	50	330
Glenalum Tunnel/Splashdam	< 28 in		18	8.2	22	28	0.87	3.2	6.1	44	79
Gilbert A/Upper Banner	< 28 in		22	13	29	33	0.76	5.2	12	46	99
Gilbert/Lower Banner	< 28 in		6	25	49	55	5.3	10	20	96	120
Douglas/Kennedy	< 28 in		15	23	35	32	2.8	11	24	54	100
Jewell/Raven	< 28 in		5	9.9	12	7.9	5.0	7.0	10	11	25
Iaeger/Jawbone	< 28 in		17	7.5	21	26	0.51	1.5	10	23	80
Lower Iaeger/Tiller	< 28 in		10	29	76	99	1.6	9.7	35	100	310
Sewell/Lower Seaboard	< 28 in		20	10	17	19	1.2	5.5	10	20	78
Welch/Upper Horsepen	< 28 in		5	19	32	23	1.4	18	39	45	59
Beckley/War Creek	< 28 in		12	8.1	15	23	1.5	4.1	11	15	87
Fire Creek/Lower Horsepen	< 28 in		8	5.5	9.1	8.3	1.3	2.1	7.1	15	21
Pocahontas No 7	< 28 in		4	23	41	35	2.7	16	44	69	75
Pocahontas No 3	< 28 in		10	5.2	17	25	0.90	1.6	2.6	32	70

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese: a. all, b. hcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4c. Thin Coal Smples, <28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quar ile ppm	Maximum ppm
							Mercury				
Redstone	< 28 in		18	0.11	0.16	0.12	0.007	0 084	0.15	0.18	0.52
Pittsburgh Roof	< 28 in		8	0.26	0.32	0.21	0.085	0.17	0.28	0.43	0.69
Pittsburgh	< 28 in		5	0.14	0.21	0.21	0.058	0 077	0.10	0.22	0.57
Harlem	< 28 in		8	0.066	0.12	0.12	0.007	0 028	0.11	0.19	0.31
Lower Bakerstown	< 28 in		18	0.14	0.24	0.29	0.003	0 093	0.19	0.25	1.3
Brush Creek	< 28 in		8	0.13	0.19	0.13	0.010	0.12	0.19	0.27	0.40
Mahoning	< 28 in		14	0.33	0.44	0.32	0.068	0.21	0.35	0.63	1.0
Upper Freeport	< 28 in	F	63	0.29	0.38	0.37	0.030	0.20	0.32	0.46	2.9
Lower Freeport	< 28 in	G	36	0.15	0.25	0.20	0.003	0.10	0.17	0.35	0.87
Upper Kittanning	< 28 in	H	35	0.14	0.27	0.27	0.003	0 060	0.24	0.38	1.3
Middle Kittanning Rider	< 28 in		8	0.42	0.53	0.37	0.14	0.25	0.48	0.65	1.3
Middle Kittanning	< 28 in	I	75	0.12	0.24	0.26	0.003	0 060	0.14	0.32	1.0
Strasburg	< 28 in		10	0.24	0.27	0.14	0.076	0.15	0.29	0.39	0.45
Lower Kittanning Rider	< 28 in		6	0.035	0.088	0.080	0.003	0 020	0.080	0.16	0.18
Lower Kittanning/No 6 block	< 28 in	J	57	0.18	0.27	0.20	0.003	0.14	0.22	0.36	0.87
Clarion	< 28 in		27	0.14	0.18	0.12	0.010	0.10	0.13	0.26	0.45
Brookville	< 28 in	L	43	0.14	0.20	0.16	0.018	0 086	0.19	0.26	0.87
No 5 Block	< 28 in		28	0.13	0.21	0.28	0.023	0 056	0.14	0.23	1.5
Upper Mercer	< 28 in		6	0.15	0.19	0.14	0.040	0 090	0.20	0.24	0.41
Lower Mercer	< 28 in		17	0.11	0.20	0.17	0.003	0 080	0.17	0.38	0.51
Quakertown	< 28 in		7	0.13	0.18	0.14	0.033	0 062	0.18	0.26	0.42
Stockton	< 28 in		11	0.15	0.21	0.18	0.020	0.11	0.18	0.21	0.67
Coalburg	< 28 in	O	76	0.12	0.17	0.12	0.010	0 074	0.15	0.23	0.59
Winifrede/Hazard	< 28 in	P	31	0.099	0.17	0.16	0.007	0 045	0.10	0.29	0.55
Lower Winifrede/Hazard	< 28 in		5	0.052	0.075	0.082	0.020	0 030	0.050	0.055	0.22
Chilton/Taylor	< 28 in		6	0.17	0.25	0.26	0.060	0 090	0.17	0.28	0.74
Fire Clay Rider	< 28 in		16	0.22	0.26	0.17	0.055	0.15	0.21	0.35	0.72
Fire Clay	< 28 in	Q	30	0.079	0.11	0.096	0.007	0 050	0.070	0.22	0.32
Cedar Grove/Whitesburg	< 28 in		23	0.16	0.25	0.26	0.020	0.12	0.21	0.27	1.1
Williamson/Amburgy	< 28 in		26	0.10	0.14	0.12	0.020	0 050	0.11	0.22	0.49
Campbell Creek/Upper Elkhorn No 3	< 28 in	T	62	0.086	0.14	0.14	0.007	0 048	0.088	0.21	0.72
Upper Elkhorn Nos 1 and 2/Powellton	< 28 in	U	55	0.12	0.19	0.15	0.007	0 055	0.17	0.26	0.65
Pond Creek	< 28 in	V	43	0.10	0.17	0.15	0.007	0 062	0.11	0.24	0.57
Matewan/Clintwood	< 28 in	W	72	0.095	0.16	0.13	0.003	0 058	0.13	0.24	0.56
Middle War Eagle/Eagle	< 28 in		11	0.077	0.11	0.090	0.010	0 048	0.093	0.16	0.29
Lit le Eagle/Dorchester	< 28 in	X	34	0.053	0.094	0.11	0.003	0 032	0.062	0.11	0.51
Lower War Eagle/Hagy	< 28 in		5	0.11	0.20	0.21	0.010	0.13	0.13	0.16	0.55
Glenalum Tunnel/Splashdam	< 28 in		18	0.13	0.21	0.16	0.003	0 073	0.21	0.36	0.48
Gilbert A/Upper Banner	< 28 in		22	0.046	0.082	0.090	0.003	0 030	0.060	0.11	0.40
Gilbert/Lower Banner	< 28 in		6	0.14	0.17	0.12	0.070	0 080	0.12	0.22	0.37
Douglas/Kennedy	< 28 in		15	0.10	0.18	0.19	0.007	0 055	0.10	0.23	0.62
Jewell/Raven	< 28 in		5	0.11	0.11	0.044	0.070	0 080	0.11	0.13	0.18
Iaeger/Jawbone	< 28 in		17	0.096	0.14	0.11	0.010	0 060	0.080	0.19	0.42
Lower Iaeger/Tiller	< 28 in		10	0.15	0.32	0.25	0.007	0 085	0.39	0.54	0.60
Sewell/Lower Seaboard	< 28 in		20	0.15	0.20	0.16	0.045	0 067	0.16	0.26	0.58
Welch/Upper Horsepen	< 28 in		5	0.20	0.32	0.32	0.070	0 070	0.19	0.45	0.81
Beckley/War Creek	< 28 in		12	0.086	0.11	0.10	0.030	0 058	0.073	0.10	0.38
Fire Creek/Lower Horsepen	< 28 in		8	0.081	0.094	0.062	0.050	0 050	0.071	0.11	0.23
Pocahontas No 7	< 28 in		4	0.065	0.065	0.006	0.060	0 060	0.065	0.070	0.070
Pocahontas No 3	< 28 in		10	0.16	0.21	0.19	0.050	0 095	0.14	0.28	0.66

Table 4. Coal quality statistics for coal beds with ≥ 5 samples for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese:
a. all, b. hcik (≥ 28 inch), and c. thin (< 28 inch) coal bed samples. [Coal bed code from table 2 if N ≥ 30; * if N < 30 for a specific parameter; N = number of samples.]

Table 4c. Thin Coal Smples, <28 inch thick.

Coal Bed Name This Study	Thickness range	Coal bed code N≥30	Manganese								
			N	Geometric mean ppm	Average ppm	Standard Deviation ppm	Minimum ppm	Lower Quartile ppm	Median ppm	Upper Quar ile ppm	Maximum ppm
Redstone	< 28 in		18	41	75	120	15	20	33	59	460
Pittsburgh Roof	< 28 in		8	15	16	6.0	6.1	14	16	18	27
Pittsburgh	< 28 in		5	12	14	6.4	3.8	11	17	18	19
Harlem	< 28 in		8	18	27	28	6.2	7.7	21	29	90
Lower Bakerstown	< 28 in		18	29	55	89	6.5	13	23	65	390
Brush Creek	< 28 in		8	15	33	53	5.2	6.3	9.3	30	160
Mahoning	< 28 in		14	12	16	15	3.3	5.7	13	24	59
Upper Freeport	< 28 in	F	61	14	21	24	1.1	7.4	12	26	140
Lower Freeport	< 28 in	G	36	24	39	42	1.2	15	23	42	170
Upper Kittanning	< 28 in	H	35	12	14	7.8	3.4	8.0	12	19	33
Middle Kittanning Rider	< 28 in		8	24	26	12	14	16	24	32	46
Middle Kittanning	< 28 in	I	75	14	20	22	1.7	8.5	15	24	140
Strasburg	< 28 in		10	27	37	32	6.3	20	31	45	120
Lower Kittanning Rider	< 28 in		6	8.5	9.9	7.0	5.8	6.4	7.2	8.4	24
Lower Kittanning/No 6 block	< 28 in	J	57	15	25	44	1.6	8.4	15	23	280
Clarion	< 28 in		27	21	28	23	5.0	12	24	41	110
Brookville	< 28 in	L	43	18	36	74	2.1	9.8	18	27	470
No 5 Block	< 28 in		28	7.1	9.6	13	3.1	4.6	6.4	9.7	71
Upper Mercer	< 28 in		6	40	63	70	11	21	44	62	200
Lower Mercer	< 28 in		17	17	30	46	4.6	8.1	15	26	190
Quakertown	< 28 in		7	12	24	38	2.6	7.4	11	15	110
Stockton	< 28 in		11	12	24	40	4.3	6.8	8.1	20	140
Coalburg	< 28 in	O	76	10	14	16	1.6	6.0	9.0	16	120
Winifrede/Hazard	< 28 in	P	31	7.7	11	9.0	1.2	3.9	6.8	17	33
Lower Winifrede/Hazard	< 28 in		5	9.2	11	7.1	3.9	4.7	12	14	21
Chilton/Taylor	< 28 in		6	13	24	31	3.3	5.9	11	24	85
Fire Clay Rider	< 28 in		16	30	64	91	4.3	10	32	68	350
Fire Clay	< 28 in	Q	30	9.7	15	17	1.9	5.0	7.1	23	83
Cedar Grove/Whitesburg	< 28 in		23	9.4	39	140	0.73	4.6	11	14	660
Williamson/Amburgy	< 28 in		26	9.8	17	34	2.2	5.6	8.4	14	180
Campbell Creek/Upper Elkhorn No 3	< 28 in	T	62	6.2	8.7	8.0	1.2	3.5	4.6	13	32
Upper Elkhorn Nos 1 and 2/Powellton	< 28 in	U	55	6.6	9.5	12	1.1	4.1	6.2	8.4	75
Pond Creek	< 28 in	V	43	13	24	40	2.1	6.6	12	21	210
Matewan/Clintwood	< 28 in	W	72	8.1	16	46	1.4	4.7	6.8	13	390
Middle War Eagle/Eagle	< 28 in		11	10	20	24	0.75	6.2	11	20	78
Lit le Eagle/Dorchester	< 28 in	X	34	7.7	11	9.8	2.0	3.6	6.7	14	42
Lower War Eagle/Hagy	< 28 in		5	11	13	8.0	4.1	11	12	14	26
Glenalum Tunnel/Splashdam	< 28 in		18	5.4	7.4	6.6	1.2	3.5	4.9	6.7	22
Gilbert A/Upper Banner	< 28 in		22	11	15	15	1.5	7.5	12	17	70
Gilbert/Lower Banner	< 28 in		6	14	14	2.7	11	13	14	16	18
Douglas/Kennedy	< 28 in		15	16	27	30	2.8	8.5	16	31	110
Jewell/Raven	< 28 in		5	19	19	4.3	12	20	21	21	23
Iaeger/Jawbone	< 28 in		17	12	18	13	1.1	7.4	16	24	48
Lower Iaeger/Tiller	< 28 in		10	25	32	21	7.3	15	34	43	74
Sewell/Lower Seaboard	< 28 in		20	20	47	78	2.1	8.0	20	36	320
Welch/Upper Horsepen	< 28 in		5	7.5	8.8	5.3	3.8	4.9	6.2	14	15
Beckley/War Creek	< 28 in		12	14	44	89	2.0	5.1	14	32	320
Fire Creek/Lower Horsepen	< 28 in		8	6.8	16	25	1.0	2.6	8.1	17	75
Pocahontas No 7	< 28 in		4	6.4	9.2	7.1	1.3	5.2	8.8	13	18
Pocahontas No 3	< 28 in		10	15	16	5.8	6.3	13	16	18	28

Table 5. Coal quality statistics for coal samples in three stratigraphic intervals (pre-SGB, SGB, post-SGB) for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese; a. all, b. thick (≥ 28 inch), and c. thin (<28 inch) coal bed samples. [N = number of samples. Coal beds in stratigraphic intervals pre-SGB, SGB, and post-SGB are listed in table 2.]

Table 5a. Coal Samples, all thicknesses.

Stratigraphic interval	Parameter	Units	N	Average	Standard Deviation	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
post-SGB	Selenium	ppm	1,333	3.2	2.2	0.20	1.8	2.6	3.8	20
SGB	Selenium	ppm	737	5.4	2.7	0.07	3.6	5.0	6.7	21
pre-SGB	Selenium	ppm	1,153	3.0	1.6	0.07	1.8	2.7	3.7	16
post-SGB	Thickness	inch	1,335	39	19	2.0	26	36	49	125
SGB	Thickness	inch	737	34	21	3.1	19	30	45	172
pre-SGB	Thickness	inch	1,155	32	16	4.0	20	31	41	128
post-SGB	Ash Yield	percent	1,244	12.06	5.15	1.70	8.44	11.00	14.70	32.03
SGB	Ash Yield	percent	710	12.01	5.83	2.00	7.70	11.13	14.80	32.90
pre-SGB	Ash Yield	percent	1,098	7.82	4.78	0.90	4.43	6.70	9.62	30.90
post-SGB	Sulfur	percent	1,297	2.88	1.51	0.39	1.80	2.69	3.73	10.40
SGB	Sulfur	percent	710	1.83	1.54	0.40	0.70	1.10	2.57	10.60
pre-SGB	Sulfur	percent	1,098	1.34	1.08	0.40	0.70	0.90	1.54	8.90
post-SGB	Pyritic Sulfur	percent	1,198	1.79	1.21	0.01	0.94	1.61	2.48	8.08
SGB	Pyritic Sulfur	percent	602	1.12	1.31	0.01	0.14	0.60	1.73	8.97
pre-SGB	Pyritic Sulfur	percent	831	0.70	0.97	0.01	0.10	0.25	0.94	7.62
post-SGB	Arsenic	ppm	1,328	30	37	0.3	8.5	19	36	410
SGB	Arsenic	ppm	734	18	30	0.4	2.9	7.5	20	300
pre-SGB	Arsenic	ppm	1,151	23	43	0.1	3.1	8.3	25	680
post-SGB	Mercury	ppm	1,335	0.26	0.23	0.003	0.11	0.20	0.33	2.9
SGB	Mercury	ppm	736	0.17	0.16	0.003	0.060	0.12	0.24	1.5
pre-SGB	Mercury	ppm	1,153	0.14	0.15	0.003	0.050	0.085	0.18	1.8
post-SGB	Manganese	ppm	1,332	27	41	0.92	10	17	29	690
SGB	Manganese	ppm	736	20	46	0.73	5.9	11	21	660
pre-SGB	Manganese	ppm	1,152	20	37	0.75	5.2	10	20	540

Table 5. Coal quality statistics for coal samples in three stratigraphic intervals (pre-SGB, SGB, post-SGB) for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese; a. all, b. thick (≥ 28 inch), and c. thin (<28 inch) coal bed samples. [N = number of samples. Coal beds in stratigraphic intervals pre-SGB, SGB, and post-SGB are listed in table 2.]

Table 5b. Thick Coal Samples, ≥28 inch thick.

Stratigraphic interval	Parameter	Units	N	Average	Standard Deviation	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
post-SGB	Selenium	ppm	942	3.1	2.1	0.20	1.8	2.6	3.7	20
SGB	Selenium	ppm	407	5.6	2.5	0.73	3.9	5.1	6.9	17
pre-SGB	Selenium	ppm	668	3.1	1.6	0.07	2.0	2.9	4.0	14
post-SGB	Thickness	inch	943	47	16	28	35	43	53	125
SGB	Thickness	inch	407	47	19	28	35	43	53	172
pre-SGB	Thickness	inch	669	42	13	28	33	39	47	128
post-SGB	Ash Yield	percent	870	11.77	4.92	2.20	8.25	10.80	14.50	32.03
SGB	Ash Yield	percent	394	12.14	5.43	2.44	8.42	11.20	14.50	31.80
pre-SGB	Ash Yield	percent	638	7.93	4.55	0.90	4.80	6.80	9.62	30.90
post-SGB	Sulfur	percent	912	2.88	1.41	0.39	1.90	2.70	3.71	8.43
SGB	Sulfur	percent	394	1.67	1.52	0.40	0.70	0.98	2.13	10.40
pre-SGB	Sulfur	percent	638	1.12	0.78	0.40	0.66	0.80	1.27	6.70
post-SGB	Pyritic Sulfur	percent	826	1.78	1.13	0.01	1.00	1.62	2.43	6.49
SGB	Pyritic Sulfur	percent	309	1.00	1.27	0.01	0.14	0.46	1.48	8.97
pre-SGB	Pyritic Sulfur	percent	440	0.47	0.67	0.01	0.09	0.19	0.55	5.43
post-SGB	Arsenic	ppm	941	24	27	0.3	7.8	15	32	320
SGB	Arsenic	ppm	407	13	19	0.6	2.5	6.2	15	180
pre-SGB	Arsenic	ppm	667	15	24	0.1	2.7	6.6	16	300
post-SGB	Mercury	ppm	943	0.25	0.21	0.003	0.11	0.20	0.32	1.7
SGB	Mercury	ppm	407	0.16	0.15	0.003	0.060	0.12	0.22	1.5
pre-SGB	Mercury	ppm	669	0.12	0.14	0.003	0.047	0.080	0.16	1.8
post-SGB	Manganese	ppm	942	27	40	0.92	11	18	29	690
SGB	Manganese	ppm	407	16	32	1.1	5.8	10	18	530
pre-SGB	Manganese	ppm	668	22	38	0.96	5.6	11	23	540

Table 5. Coal quality statistics for coal samples in three stratigraphic intervals (pre-SGB, SGB, post-SGB) for selenium, thickness, ash yield, sulfur, pyritic sulfur, arsenic, mercury, and manganese; a. all, b. thick (≥ 28 inch), and c. thin (<28 inch) coal bed samples. [N = number of samples. Coal beds in stratigraphic intervals pre-SGB, SGB, and post-SGB are listed in table 2.]

Table 5c. Thin Coal Smples, <28 inch thick.

Stratigraphic interval	Parameter	Units	N	Average	Standard Deviation	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
post-SGB	Selenium	ppm	391	3.3	2.3	0.43	1.9	2.8	3.9	14
SGB	Selenium	ppm	330	5.2	2.8	0.07	3.2	4.6	6.4	21
pre-SGB	Selenium	ppm	485	2.8	1.7	0.07	1.7	2.4	3.4	16
post-SGB	Thickness	inch	392	20	5.9	2.0	16	21	25	28
SGB	Thickness	inch	330	17	6.1	3.1	12	18	22	28
pre-SGB	Thickness	inch	486	18	6.0	4.0	13	19	24	28
post-SGB	Ash Yield	percent	374	12.74	5.59	1.70	9.01	11.44	15.68	31.20
SGB	Ash Yield	percent	316	11.85	6.29	2.00	7.11	11.00	15.23	32.90
pre-SGB	Ash Yield	percent	460	7.66	5.09	0.90	4.12	6.40	9.61	29.55
post-SGB	Sulfur	percent	385	2.86	1.72	0.40	1.50	2.60	3.79	10.40
SGB	Sulfur	percent	316	2.02	1.55	0.41	0.80	1.50	2.91	10.60
pre-SGB	Sulfur	percent	460	1.64	1.34	0.40	0.71	1.03	2.18	8.90
post-SGB	Pyritic Sulfur	percent	372	1.81	1.37	0.01	0.76	1.58	2.58	8.08
SGB	Pyritic Sulfur	percent	293	1.24	1.35	0.01	0.15	0.82	2.00	8.67
pre-SGB	Pyritic Sulfur	percent	391	0.95	1.18	0.01	0.12	0.41	1.53	7.62
post-SGB	Arsenic	ppm	387	44	50	0.7	12	30	55	410
SGB	Arsenic	ppm	327	24	39	0.4	3.6	11	28	300
pre-SGB	Arsenic	ppm	484	34	57	0.4	4.0	13	42	680
post-SGB	Mercury	ppm	392	0.28	0.28	0.003	0.095	0.21	0.37	2.9
SGB	Mercury	ppm	329	0.19	0.17	0.003	0.070	0.15	0.26	1.5
pre-SGB	Mercury	ppm	484	0.16	0.15	0.003	0.050	0.10	0.23	0.81
post-SGB	Manganese	ppm	390	29	46	1.1	8.5	16	28	460
SGB	Manganese	ppm	329	25	58	0.73	6.1	11	22	660
pre-SGB	Manganese	ppm	484	17	34	0.75	4.7	8.7	18	390

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
Volume		
Liter (L)	33.82	ounce, fluid (fl. oz)
Liter (L)	2.113	pint (pt)
Liter (L)	1.057	quart (qt)
Liter (L)	0.2642	gallon (gal)
Liter (L)	61.02	cubic inch (in^3)
Mass		
Gram (g)	0.03527	ounce, avoirdupois (oz)
Kilogram (kg)	2.205	pound avoirdupois (lb)

Selenium Concentrations in Middle Pennsylvanian Coal-Bearing Strata in the Central Appalachian Basin

By Sandra G. Neuzil[1], Frank T. Dulong[1], C. Blaine Cecil[1], Nick Fedorko[2], John J. Renton[3], and D. K. Bhumbla[4]

Executive Summary

This report provides the results of a reconnaissance-level investigation of selenium (Se) concentrations in Middle Pennsylvanian coal-bearing strata in the central Appalachian basin. Bryant and others (2002) reported enrichments of Se concentrations in streams draining areas disturbed by surface mining relative to Se concentrations in streams that drain undisturbed areas; the study was conducted without the benefit of data on Se concentrations in coal-bearing strata prior to anthropogenic disturbance. Thus, the present study was conducted to provide data on Se concentrations in coal-bearing strata prior to land disturbance. The principal objectives of this work are: 1) determine the stratigraphic and regional distribution of Se concentrations in coal-bearing strata, 2) provide reconnaissance-level information on relations, if any, between Se concentrations and lithology (rock-type), and 3) develop a cursory evaluation of the leachability of Se from disturbed strata. The results reported herein are derived from analyses of samples obtained from three widely-spaced cores that were collected from undisturbed rock within a region that has been subjected to extensive land disturbance principally by either coal mining or, to a lesser extent, highway construction. The focus was on low-organic-content lithologies, not coal, within the coal-bearing interval, as these lithologies most commonly make up the fill materials after coal mining or in road construction.

The results and interpretations of the present study are summarized as follows:

- The precision of the analytical method used in this study to determine Se concentrations in rock samples is consistent with the precision as reported by ASTM (The American Society for Testing and Materials, ASTM 3052, standard method for the determination of Se in rock samples, 95 percent confidence interval (CI 95%) = 0.9 µg/g at the 1 µg/g (1 part per million, ppm) level of concentration). The precision of ASTM 3052 is likely to decrease as the concentration of Se decreases below 1 µg/g.

- The average Se concentrations in coal-bearing strata in the central Appalachian basin are similar to the average Se concentrations reported for equivalent lithologies (Horn and Adams, 1966 and references therein). Therefore, the average Se concentrations in the various

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lithologies investigated in the present study are not anomalous when compared to values reported in the literature.

- The mean Se concentrations in the higher stratigraphic interval (Stockton A coal bed, lower Allegheny Formation, down to the Chilton A coal bed, middle Kanawha Formation) are consistently higher than the mean Se concentrations in the lower stratigraphic interval (Chilton A coal bed down to the Fire Clay coal bed in the middle Kanawha Formation) in each of the three cores that were evaluated. The apparent stratigraphic trend in Se concentrations appears to mimic the stratigraphic trend of Se concentrations in coal beds reported by Neuzil and others (2005).

- There is no demonstrable regional variation (trend) in Se concentrations.

- With the possible exception of higher Se concentration in siltstone, the mean and range of selenium concentrations is similar among four dominant lithologies (claystone, shale, siltstone, and sandstone).

- Se concentrations are not consistently correlated with a specific mineral or major element.

- Se concentrations were determined in selected coal-bed roof, parting, and floor samples from one core. The mean values of Se concentrations for each of these three types of samples are statistically equal.

- Se concentrations in the selected roof, parting and floor samples are not statistically correlated with total sulfur concentrations (a proxy for the mineral pyrite, FeS_2). Therefore, it is unlikely that a majority of the Se is associated with pyrite in these samples.

- Se concentrations in the selected roof, parting, and floor samples correlate with the loss on ignition analyses (a proxy for organic matter concentrations). The loss on ignition correlation suggests that most of the Se in roof, parting, and floor samples analyzed is organically bonded. Rates of organically bonded Se dissolution are likely to be slow and are probably controlled by relatively slow rates of chemical oxidation of the host organic matter.

- Cursory leaching studies indicate that Se concentrations in rock samples are not correlated with Se concentrations in water leachates derived from splits of the same rock samples. Therefore, total Se, as determined in whole-rock samples, may not be a reliable indicator of water soluble Se. Consequently, leach testing, rather than total Se concentrations in rock, may be a more useful predictor of potential stream contamination following land disturbance.

- Although the readily soluble fraction of the total Se in coal-bearing strata is unknown, the cursory study of sequential water leaching conducted in the present investigation indicates that readily soluble Se may be rapidly removed from rock debris following disturbance of strata.

On the basis of the present study, the average concentrations of Se in Middle Pennsylvanian coal-bearing strata in the central Appalachian basin are not anomalous when compared to published values for similar rock types. In addition, the average concentrations of Se indicate that if regional trends exist, such trends are below the detection limits of the methods used in this study. Also, there is no apparent association of Se with a specific mineral or a specific rock type (claystone, shale, siltstone, or sandstone) with the possible exception of Se enrichment in certain siltstone and coal-bed roof, parting, and floor samples. Leach testing methods, rather than analyses of total Se content of rocks, may provide the most accurate assessment of the potential for Se mobilization and stream contamination as a result of land disturbance.

Introduction

   The upper limit of total Se concentration in streams recommended by EPA in order to protect aquatic life is 5 micrograms per liter (µg/L, parts per billion, or ppb). Bryant and others (2002) reported that concentrations of Se in streams draining areas disturbed by surface mining of coal in the central Appalachian basin were higher (median 12 µg/L) in comparison to streams draining undisturbed areas (median 1.5 µg/L). However, a general lack of data on Se concentrations in coal-bearing strata precluded the attribution of Se concentrations in streams to specific rock types, stratigraphic intervals, or specific areas subjected to land disturbance. To address any potential correlations between bed rock geology, dissolution of Se following land disturbance, and subsequent increases in Se concentrations in streams, the U.S. Geological Survey (USGS), in cooperation with the West Virginia Geological and Economic Survey (WVGES) and West Virginia University (WVU), initiated a study to evaluate Se concentrations in coal-bearing strata (not including the coal beds) in the central Appalachian region.

   In a companion study, Neuzil and others (2005) used data from the USGS National Coal Resources Data System to evaluate Se concentrations in Pennsylvanian-age coal beds in the Appalachian region. Their study indicates that Se concentrations in Middle Pennsylvanian age coal beds (the principal stratigraphic interval of mountain-top-mining at the time of their report) are somewhat enriched in Se (median 5 ppm Se, for 737 samples) relative to older and younger coal beds (median 3 ppm Se, for 1486 samples). The overall conclusions of the study by Neuzil and others (2005) are consistent with earlier observations by Gluskoter and others (1977) that Se is enriched in coal beds relative to host strata and relative to the average abundance of Se in the earth's crust. The average Se concentration of upper continental crust is poorly constrained. However, Rudnick and Gao (2003) suggest a value of 0.09 ppm Se based on few data.

   Although Se concentrations in coal beds world wide (Yudovich and Ketris, 2006), in the United States (Coleman and others, 1993), in eastern Kentucky (Eble and Hower, 1997), and in West Virginia (WVGES, 2002) are relatively well known, systematic studies of Se in strata associated with coal beds have been minimal. Therefore, the present study was designed to develop a preliminary understanding of Se concentrations in coal-bearing strata in the central Appalachian basin. This report focuses on Middle Pennsylvanian strata where anthropogenic activities such as surface mining and highway construction have either disturbed or may disturb large volumes of rock.

   The present study was undertaken to begin developing a data base that can be used in the assessment of the effects of land disturbance on Se concentrations in surface streams, as suggested by Bryant and others (2002). The current study is a first-stage in the possible development of a comprehensive data base, and as such this report is preliminary in nature. Far more data will be required in order to conduct a comprehensive assessment of Se concentrations in Pennsylvanian age coal-bearing strata, comparable to the report by Neuzil and others (2005) on Se in coal beds. The objectives of the present study were to: 1) evaluate the spatial variation of Se, in coal-bearing strata in the central Appalachian basin, 2) make a preliminary comparison of Se concentrations in coal-bearing strata of the region relative to average concentrations of Se in sedimentary strata, as reported in the literature, and 3) investigate the mobilization of Se by water from disturbed coal-bearing strata. For the purposes of this report, spatial variation refers to both stratigraphic variation and regional variation of Se concentrations in coal-bearing strata. Stratigraphic trends refer to any vertical trends in Se concentrations over hundreds of feet of coal-bearing strata. Regional variation

relates to regional trends in Se concentrations over tens to hundreds of square miles. Three widely spaced cores that were designated as USGS 9, USGS 11, and USGS 12 were collected, sampled, and the samples analyzed, as part of this regional study (fig. 1). The principal coal-bed stratigraphic intervals identified in each of the three cores are shown in Appendices A1, A2, and A3. The second objective is intended to discern if Se in the coal-bearing strata of the central Appalachian region is in any way anomalous when compared to similar sedimentary rocks. The third objective is to investigate whether there is any simple analysis that can be used to help predict any potential for elevation of Se in streams as a result of land disturbance.

Acknowledgments

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Methods and Analyses

Coring

The cores discussed in this report were part of a coring program that was developed to evaluate geologic controls on mine-drainage water quality, principally acid drainage. The total coring program consisted of eleven cores collected from both the northern- and southern-coal fields of West Virginia (fig. 1). One additional core was collected from Pennsylvanian strata in the Illinois basin. The cores were designated as USGS cores and they were numbered consecutively from one (1) through twelve (12) in the order that they were drilled. Preliminary results of the larger acid drainage study can be found in Dulong and others (2002). Cores included in this report are limited to those analyzed for Se (USGS 9, USGS 11, and USGS 12). The locations of the three cores were selected to provide a cursory evaluation of spatial variations (stratigraphic and regional) of Se in Middle Pennsylvanian coal-bearing strata in the central Appalachian basin (fig. 1). All three cores intercepted a stratigraphic interval in the Middle Pennsylvanian from the base of the Stockton A coal bed in the lower Allegheny Formation to the top of the Fire Clay coal bed in the middle Kanawha Formation. All coal beds intercepted in each core are listed in Appendices A1, A2, and A3.

Cores were obtained using standard coal exploratory wireline coring methods, producing a nominal 2 inch diameter core. Professional geologists from the WVGES logged all cores in the field as they were collected. Lithology terminology and abbreviations, as used by the WVGES for lithologic descriptions, are contained in Appendix A4. Core descriptions of USGS 9, USGS 11, and USGS 12 are contained in Appendices A5, A6, and A7. In addition, the three core holes were logged using standard coal-field geophysical logging that included density and natural gamma ray logs for USGS 9 (Appendix A8), USGS 11 (Appendix A9), and USGS 12 (Appendix A10). Comparison of geophysical logs with geological logs assured the accuracy of both core recovery and depth assignments to specific stratigraphic units such as coal beds.

Each core of coal-bearing strata was boxed by the geologist on site, and then sent to the WVGES core warehouse where they were sampled for Se analyses. Cores of coal beds, including partings within the coal beds, as well as six inches of strata above and below the coal (roof-rock and floor-rock respectively) were removed from the core at the coring site, placed in core boxes, and sent to the WVGES coal laboratory for standard coal analyses. Standard coal analyses by the WVGES generally include petrography, elemental analyses, forms of sulfur, and ash content. Coal

analyses are not considered in this report because coal is removed as part of the mining process and should not, therefore, represent a significant source of Se in disturbed areas. Occasionally isolated blocks of coal in sandstone channel complexes and strata between coal beds may be encountered and included in fill material. In the present study the roof, parting, and floor samples from USGS 9 were analyzed for total sulfur, ash content, and Se content.

Core Sampling

Costs prohibited analysis of entire cores. Therefore, sets of samples were selected from the cores to assure the following: 1) representative samples of all lithologies were analyzed, 2) samples of lithologies were random, and 3) roof, parting, and floor lithologies were adequately sampled. Four different sampling protocols were used: 1) selection of one-foot increment samples on the basis of lithology (USGS 9), 2) collection of one-foot samples every ten feet (USGS 9, USGS 11, and USGS 12), 3) collection of samples of roof, parting, and floor associated with coal-beds (USGS 9), and 4) selection of one-foot and partial-foot thick samples close to coal beds (USGS 9). The four sampling protocols were used to collect samples from core USGS 9 whereas only the second sampling protocol was used to collect samples from cores USGS 11 and USGS 12. Samples for analyses were obtained by splitting the core lengthwise with a diamond rock saw and taking the appropriate depth increment.

The first sampling method, used exclusively on core USGS 9, was based on lithologies. One hundred (100) one-foot increment samples representing the four principal lithologies of the core (9 claystone and mudstone, 20 shale, 23 siltstone, and 48 sandstone) were selected. The lithologic description of USGS 9 (Appendix A5) indicates a total thickness of 105 ft claystone and mudstone, 235 ft shale, 235 ft siltstone, and 1069 ft sandstone, or a distribution of the four lithologies of approximately 6, 14, 14, and 65 percent respectively. The samples selected for lithology are referred to as lithology samples, indicated as USGS 9-LITH. This sampling method assured that representative samples of the various lithologies, in proportion similar to their abundance in the entire core, were analyzed.

The second core sampling method, which was used on all three cores, consisted of collecting a one-foot increment within each ten-foot interval of the core. These samples are referred to as increment samples, indicated as USGS 9-10-ft, USGS 11-10-ft, and USGS 12-10-ft for the three cores. This method assured randomness of sampling of each core without bias toward any parameter except depth from surface.

The third sampling method involved selection of roof samples (generally six-inch increments of strata above coal beds), parting samples (variable thicknesses of rock within coal beds), and floor samples (generally six-inch increments of strata below coal beds) from core USGS 9. These samples, collectively referred to as RPF and indicated as USGS 9-RPF, were intentionally biased toward the strata that immediately overlie, are contained within, and underlie coal beds. The RPF samples were analyzed in order to evaluate the common perception that coal bed roof, parting, and floor strata tend to be relatively enriched in Se.

The fourth sampling method selected additional samples close to coal beds in core USGS 9. Some of these samples were one foot thick (indicated as 1-ft) and some were less than one foot thick (indicated as p-ft, for 'partial-foot'). Throughout this report the 1-ft samples selected close to coal beds, as well as the interval samples (one-foot thick sample collected in each ten-foot interval

of the core) are included in USGS 9-10-ft. Occasionally in this report the p-ft samples are also included in USGS 9-10-ft data analyses.

Selenium Analyses of Core Samples

Each one-foot increment of core was cut longitudinally with a saw so that about one quarter of the core was removed. These quarter-core splits were reduced in size to ¼ to ½ inch pieces with a jaw crusher. The resulting material was quartered and three parts archived in plastic sample bags. The remaining quarter was further reduced to about 1/8 inch pieces with a mortar and pestle and then ground in a shatterbox pulverizer for no more than 5 minutes to a size that passed through a 60 mesh screen.

The prepared samples were submitted to the analytical laboratory in the West Virginia University, College of Agriculture, Division of Plant and Soil Sciences, where they were analyzed for Se using the graphite furnace-atomic absorption (GFAA) method, modified ASTM 3052 [D1] (ASTM Method 3052). One quarter gram (0.25 g) of sample was weighed and placed in a fluorocarbon reaction vessel with a pressure relief valve fitted with a fluorocarbon membrane. The reaction vessel could withstand a pressure of 500 PSI. The sample was then digested in 3 milliliters (ml) of hydrofluoric acid (HF) and 9 ml of nitric acid (HNO_3) for 10 minutes in a microwave until all material appeared to be in solution. Subsequently, the digestion liquors were treated with 25 ml of saturated boric acid solution and then brought to 50 ml total volume by adding distilled water. The resultant solution was then filtered through Whatman #42 filter paper and analyzed for Se using the graphite furnace-atomic absorption spectrometer equipped with a Zeeman background correction system.

Results of the Se analyses of rock samples from all three cores are shown for USGS 9-LITH (Appendix B1), USGS 9-10-ft (Appendix B2), USGS 11-10-ft (Appendix B3), and USGS 12-10-ft (Appendix B4). Selenium determinations that were below the limits of detection (10 μg/kg) were reported as ND (not detected). It is a common statistical practice to assign a value equal to half the detection limit to samples with analyses below the detection limit. In this report, however, for statistical analyses of data sets and graphical illustration, ND data were assigned a value of zero (0). A third of the samples have a Se concentration greater than 1,000 μg/kg, which is two orders of magnitude greater than the lower detection limit.   Thus, whether a value of zero or a value equal to half the detection limit (5 μg/kg) is assigned to samples with Se concentration below the detection limit will make little difference in statistical calculations and comparisons. The difference is discussed further under the heading "Results – Frequency Distribution of Selenium Concentrations in All Cores."

Analyses of Core Samples for Mineralogy and Major Element Oxides

A semi-quantitative estimate of the major-phase mineralogy was determined by X-ray diffraction (XRD) on all one-foot increment samples at WVU laboratories. The XRD method is semi-quantitative. Low values, less than approximately 5 percent, should be used with caution. The major mineralogical phases include chlorite, kaolinite, quartz, orthoclase (feldspar), calcite, pyrite, siderite, dolomite, illite, and albite (feldspar). In addition to mineralogy, the major element oxides were determined by X-ray fluorescence (XRF) at WVU laboratories. XRF is a semi-quantitative method. The major oxides include MnO, K2O, SiO2, Al2O3, SO2, Fe2O3, Na2O, MgO, TiO2, CaO, and P2O5. Results for XRD mineralogy and XRF major element oxides are

reported for USGS 9-LITH (Appendix B5), USGS 9-10-ft (Appendix B6), USGS 11-10-ft (Appendix B7), and USGS 12-10-ft (Appendix B8).

Analyses of Total Sulfur and Loss on Ignition in Coal-Bed Roof, Parting, and Floor Samples

In addition to standard coal analyses, which include total sulfur (dry basis) and ash (750º C, dry basis), the roof, parting, and floor samples from USGS 9 were analyzed for Se content. Loss on ignition (LOI) was calculated from percent ash, LOI = (100 – percent ash). Results of the analyses of roof, parting and floor samples from USGS 9 are shown in Appendix B9. Coal analyses are not considered in this report because coal is removed as part of the mining process, and should not represent a significant source of Se in disturbed areas.

Leach Tests: Saturated Paste Extract (SPE) and Sequential Water Extraction (SWE)

In addition to the analysis of total Se in selected core samples, some of the ground rock samples were analyzed for soluble Se by an adaptation of a method used in analyses of soluble salts in soils, a method known as saturated paste extract (SPE) (Rhoades, 1982). The SPE analyses were used to estimate the amount of Se that might be available for relatively rapid dissolution following land disturbance and reclamation.

The SPE Se determinations were conducted as follows on samples from USGS 9-10-ft, USGS 11-10-ft, and USGS 12-10-ft. A saturation paste of the sample was prepared by adding 11 ml deionized water to a 50-ml fluorocarbon centrifuge tube and then adding 30 g of sample. The mixture was allowed to set overnight, and then shaken for two (2) hours on a wrist-action shaker at a speed of 10. After shaking, the mixture was centrifuged at 5000 rpm for 25 minutes in an IES-Centram p4r centrifuge. The liquid obtained after centrifugation was filtered through a 0.45 μm cellulose nitrate membrane filter. The filtrate was analyzed for Se using the standard GFAA method on a Perkin-Elmer 4000 atomic absorption spectrophotometer. Results for the SPE leach tests are presented for USGS 9-10-ft (Appendix B10), USGS 11-10-ft (Appendix B11), and USGS 12-10-ft (Appendix B12).

A second SPE extraction was conducted on 7 of the 87 samples from USGS 11-10-ft. Following the initial saturated paste extract, the residual material was extracted a second time. The first extract (SPE) was labeled "A" (SPE-A) and the second extract was labeled "B" (SPE-B) (Appendix B11).

Selected samples from USGS 11-10-ft were subjected to sequential water extraction (SWE) of Se. Sequential water extractions were run on 44 fresh samples, designated A, some of which were splits derived from samples that were subjected to SPE. For the SWE samples, 10 ml of deionized water was added to 5 g of sample. The mixture was allowed to set overnight, and then shaken for two hours at a speed of 10 on a wrist-action shaker. The mixture was centrifuged at 5000 rpm for 25 minutes in an IES-Centram p4r centrifuge, and then filtered through a 0.45 μm cellulose nitrate membrane filter. The filtrate was then analyzed. Subsequent sequential extractions were conducted by adding an additional 10 ml of water to the solid residue, followed by repetition of all other steps, for up to six sequential extractions (2nd through 7th extracts). For 15 of the 44 samples, a second split was leached, resulting in analyses of duplicate samples, labeled "B." Results for all SWE analyses for USGS 11-10-ft are presented in Appendix B13.

Results

Estimates of Analytical Precision

The American Society for Testing and Materials (ASTM) standard method for the determination of Se in rock samples (ASTM 3052 D1) was used in this study. ASTM evaluated the 95 percent confidence interval (CI 95%) for the method by conducting replicate analyses of National Institute of Standards and Testing (NIST) standard reference material (SRM) 2704, Buffalo River Sediment. NIST reports a Se concentration of 1.1 µg/g (ppm) in SRM 2704 but does not certify this value, possibly because only one analytical method was used to determine Se. ASTM analyzed SRM 2704 a number of times for 13 elements, including Se (n = 4), and reported a mean Se concentration of 1.13 µg/g (ppm) with a CI 95% of 0.9 µg/g (table 1). Thus, the determination of Se by the ASTM 3052 standard method may be relatively imprecise at the 1 µg/g (ppm) concentration level and below.

In the present study, the precision of the ASTM 3052 method for the determination of Se was estimated on the basis of analyses of replicate samples from USGS 9. Each of 12 one-foot increment samples from USGS 9 was analyzed twice, once as part of the lithology sampling, USGS 9-LITH (Appendix B1), and once as part of the 10-foot increment sampling, USGS 9-10-ft (Appendix B2). Inspection of the two sets of analyses indicate that the Se values from USGS 9-LITH samples are, in general, lower than the Se values for the USGS 9-10-ft samples (table 2).

As a result of the apparent differences in the duplicate analyses for Se in the twelve coincident samples from USGS 9, the twelve coincident samples were used to estimate the precision of the analytical method. In order to develop a data set that could be evaluated statistically, each of the twelve USGS 9-10-ft samples that was a duplicate of a USGS 9-LITH sample was sub-sampled two additional times. These sub-samples were then digested, and each digestion was analyzed three times. Thus, each of the twelve USGS 9-10-ft samples was sub-sampled a total of three times, designated as A, B, and C. The sub-samples were digested and each of the digestion liquors was analyzed in triplicate (identified as 1, 2, and 3). The data are shown in Appendix B14.

An estimate of the precision of the ASTM 3052 analytical method was based on statistical evaluation of the Se concentration data from three sub-samples and 3 replicate analyses of each sub-sample for 12 USGS 9-10-ft samples, which are coincident with 12 samples from USGS 9-LITH. The mean, standard deviation, number of analyses (N=9), and the 95 percent confidence interval (CI 95%) for the mean are shown in table 3 for the 12 coincident samples. A normalized metric was calculated in order to compare the 95 percent confidence intervals for mean Se concentrations among the 12 coincident samples in USGS 9, where replicate analyses may vary by two orders of magnitude (Appendix B14) and mean Se concentrations (table 3) are less than 1000 µg/kg (1 ppm), with the 95 percent confidence interval reported by ASTM, where the mean Se concentration (table 1) is greater than 1 µg/kg (1 ppm). The normalized metric, used here to indicate precision of results, is the CI 95% divided by the mean Se concentration, for each sample. The CI 95% reported by ASTM was divided by the mean reported by ASTM yielding a value of 0.80 (table 1). In the present study, for each sample, the CI 95% was divided by the mean and the 12 resultant values were averaged giving the lab's precision of the ASTM 3052 method as 0.80 (table 3). Thus, the precision of analyses by the ASTM 3052 method, estimated by the metric CI

95% / mean in the present study is similar to the precision reported by ASTM, even though the Se concentrations are lower in the present study (table 3) compared to the ASTM study (table 1).

Core Comparisons: a Test for Spatial Variation in Selenium Concentrations in Middle Pennsylvanian Coal-Bearing Strata

A principal objective of the present study was to evaluate spatial variation of Se concentrations in coal-bearing strata in the central Appalachian basin. Spatial variation in Se concentrations, as used in this report, refers to both stratigraphic variation (vertical trends) and regional variation (lateral trends).

Stratigraphic Variation

An analysis of stratigraphic variation of Se in Middle Pennsylvanian strata included the lower part of the Allegheny Formation down through the middle of the Kanawha Formation (Appendices A1, A2, A3). A stratigraphic comparison of Se concentration data was made within each of the three cores that were evaluated in the present study. The stratigraphic comparisons were based on the mean and 95% confidence interval of two specific stratigraphic intervals in each of the three cores. The two stratigraphic intervals were selected on the basis of a visual inspection of the data derived from analyses of samples from the first core that was analyzed, USGS 9-LITH (fig. 2). Visual inspection of the Se concentration values in USGS 9-LITH indicated that Se concentrations were commonly above the limits of detection from the Stockton A coal bed down to the Chilton A coal bed, whereas Se concentrations were commonly below the limits of detection from the Chilton A coal bed down to the Fire Clay coal bed. Thus, the two stratigraphic intervals consist of an upper interval from the base of the Stockton A coal bed down to the top of the Chilton A coal bed, and a lower interval from the base of the Chilton A coal bed down to the top of the Fire Clay coal bed. The plots of Se concentrations versus depth for the other core data sets are presented for USGS 9-10-ft (fig. 3), USGS 11-10-ft (fig. 4), and USGS 12-10-ft (fig. 5).

The univariate statistics for the two stratigraphic intervals for each core are presented in table 4. Comparisons of mean Se concentrations and their respective CI 95% for each stratigraphic interval are shown in figure 6 for each core. The rank order of the means of Se concentrations is always greater in the upper stratigraphic interval relative to the lower stratigraphic interval (table 4). However, only in USGS 9 is the mean value for Se concentration in the upper stratigraphic interval (from the bottom of the Stockton A coal bed down to the top of the Chilton A coal bed) statistically greater than that for the lower stratigraphic interval (from the bottom of the Chilton A coal bed down to the top of the Fire Clay coal bed). Statistical analyses of both samplings of USGS 9 (-LITH and -10-ft) indicate that the mean Se values in strata overlying the Chilton A Coal bed (553 and 666 µg/kg Se, respectively) are greater than the mean Se values in strata that underlie the Chilton A coal bed (64 and 329 µg/kg Se, respectively) (table 4). In contrast, based on t-tests, there are no statistical differences between the means of Se concentrations in the two stratigraphic intervals in either USGS 11-10-ft or USGS 12-10-ft (table 4). The apparent stratigraphic trend in Se concentrations in coal-bearing strata, exclusive of coal, in USGS 9 is consistent with stratigraphic trends in Se in coal beds as reported by WVGES (2002) for West Virginia and Neuzil and others (2005) for the Appalachian Plateau region. Although the rank-order of Se values in the upper and lower stratigraphic interval is consistent among the three cores, stratigraphic trends in Se concentrations cannot be verified statistically in either USGS 11 or USGS 12 for the stratigraphic intervals considered. Thus, a stratigraphic trend in Se concentrations in rock in the Middle Pennsylvanian coal-bearing strata cannot be stated with certainty on the basis of the present study.

Regional Variation

Regional variation was tested on the basis of three cores, USGS 9, USGS 11, and USGS 12 spaced approximately 50 km apart (fig.1). Regional variation among cores was evaluated by a statistical t-test comparison of mean Se concentrations (µg/kg) for each of the two stratigraphic intervals. The results are summarized in table 5. The rank order of the mean Se concentrations in the upper stratigraphic interval is USGS 9-10-ft > USGS 9-LITH > USGS 12-10-ft > USGS 11-10-ft. Statistical t-tests show that USGS 9-10-ft is greater than both USGS 12-10 ft and USGS 11-10 ft and that USGS 9-LITH is greater than USGS 11-10-ft. Otherwise, mean Se concentrations are statistically equal. For the lower stratigraphic interval, the rank order of the mean Se concentrations is USGS 9-10-ft > USGS 12-10-ft > USGS 11-10-ft > USGS 9-LITH. Statistical t-tests show that mean Se concentration in USGS 9-10-ft samples is greater than mean Se concentration in USGS 9-LITH samples. All other mean Se concentrations are equal for the lower stratigraphic interval. There are no differences in mean Se concentration between any two cores that hold for both the upper and lower stratigraphic interval. On the basis of data derived from analyses of samples obtained from the three cores that were tested in this study, there are no apparent regional variations (trends) in Se concentrations.

Frequency Distribution of Selenium Concentrations in Three Cores

The univariate statistics and frequency distribution information for Se concentrations in all 1-foot increment samples collected at 10-foot intervals (USGS 9-10-ft, USGS 11-10-ft, and USGS 12-10-ft), are shown in table 6. The Se values for USGS 9-LITH were not used for this analysis because of the different sampling method. The two highest Se values, 6820 and 3300 µg/kg, are considered high outlier values because they are each approximately twice the value of the next highest Se concentration (table 6). These samples were dropped in order to examine the frequency distribution of Se concentrations in the remaining 234 samples collected at 10-foot intervals (fig. 7). Concentrations below the limit of detection (ND) account for 33 percent of all Se concentration values. Sixty eight percent of the values are less than 500 µg/kg, and eighty nine percent of the values are below 1000 µg/kg. Therefore, the Se data appear to have a log normal distribution, which is typical for trace element geochemical data. Whether Se concentrations below the detection limit are assigned a value of zero or 5 µg/kg (half the limit of detection), the mean and standard deviation change by 2 µg/kg, which is less than 1 percent of the value of the mean and standard deviation (table 6). In this study a value of zero was assigned to samples below the detection limit, which made little overall difference to the statistics.

Selenium Concentrations and Dominant Lithologies (Rock Types)

Four dominant rock types in USGS 9 were sampled for USGS 9-LITH in proportions similar to their total thickness in the entire USGS 9 core (Appendix A5). The proportions of the four dominant rock types in core USGS 9 and the two sample sets taken from the core are as follows: claystone and mudstone, shale, siltstone, and sandstone each represent 6, 14, 14, and 65 percent of core USGS 9; 9, 20, 23, and 48 percent of samples in USGS 9-LITH; and 14, 5, 10, and 71 percent of samples in USGS 9-10-ft. The mean Se concentrations and 95 percent confidence intervals (µg/kg) within each of the four lithologies were used to evaluate the relation, if any, between rock-type and Se concentrations. Univariate statistics and comparisons among dominant lithologies were conducted on the two data sets from USGS 9, USGS 9-LITH samples selected by lithology and USGS 9-10-ft samples collected every ten feet, and are summarized in table 7.

The mean Se concentration ± the 95 percent confidence interval for the four dominant lithologies from USGS 9-LITH and USGS 9-10-ft are shown in figure 8 and figure 9. Among the four dominant rock types in the two samplings of USGS 9, the rank order of the mean Se concentrations are higher in siltstone than in claystone, shale, or sandstone. However, t-test statistical analyses show that only mean Se concentrations in siltstone are higher than in claystone for both samplings (table 7).

Selenium Concentrations in Roof, Parting, and Floor samples

T-test analyses of the Se concentration data derived from roof (rock immediately above coal beds), parting (rock within coal beds), and floor (rock immediately below coal beds) samples from USGS 9 indicate that the mean Se concentrations in coal-bed roof, parting, and floor samples are statistically equal (table 8). Because the mean Se concentrations in roof, parting, and floor samples are equal, the three data sets can be combined and referred to as RPF. The univariate statistics for USGS 9-RPF samples are shown in table 9. The mean Se concentration for all USGS 9-RPF samples was compared to the mean Se concentrations of the four dominant lithologies data sets derived from each of two samplings of USGS 9 (figs. 10 and 11). The statistical t-test comparisons of RPF samples with samples of four dominant lithologies in USGS 9-LITH and USGS 9-10-ft are summarized in table 10.

Results show that RPF samples are likely to have Se concentrations that are similar to siltstones, but greater than claystones, shales, and sandstones. The statistical similarity between RPF samples and shale samples from USGS 9-10-ft is due to the large dispersion of the mean, indicated by the large 95 percent confidence interval, for the few (N = 4) shale samples (table 7).

The statistical t-test evaluation comparing mean Se concentrations separately in each of the roof, parting and floor sample data sets with each of the four dominant rock types (lithologies) from USGS 9-LITH samples (fig. 8) and USGS 9-10-ft (fig. 9) are summarized in table 10. The results are similar to those comparing RPF samples to the four dominant lithologies. Roof and floor samples have Se concentrations similar to siltstone samples whereas roof, parting, and floor samples have Se concentrations greater than claystone, shale, and sandstone samples for USGS 9-LITH (fig. 8; table 10). The rank-order of the means for roof, parting, and floor samples and the four dominant lithology types of samples from USGS 9-LITH is as follows: parting > floor > roof > siltstone > sandstone > shale > claystone (tables 7 and 8). For USGS 9-10-ft, differences in the mean Se concentration are not discernible between roof samples and the four dominant lithologies, whereas parting and floor samples tend to have Se concentrations greater than claystone and sandstone samples and similar to shale and siltstone samples (fig. 9; table 10). The rank order of the means for roof, parting, and floor samples and the four dominant lithologies in USGS 9-10-ft is as follows: parting > siltstone > floor > roof > sandstone > claystone > shale (tables 7 and 8).

Relation Between Selenium, Mineralogy, and Major Element Oxides Concentrations

Pearson's product moment correlation coefficients were calculated between Se and each mineral and major element oxide concentration in each core sampling. Few significant correlations (at the 5 percent level of significance) were found. There are no significant correlations of Se with pyrite or Fe_2O_3 in any of the four core samplings. More than half of the samples in each of the four core sample sets have zero values (below detection limit) for calcite, pyrite, and sulfur (Appendices B5, B6, B7, B8).

Selenium concentration is significantly correlated with siderite in samples from USGS 9-LITH (fig. 12). Selenium concentrations for samples from USGS 9-10-ft are not significantly correlated with any mineral or major element.

Se concentrations in samples from USGS 11-10-ft include one point with high Se, calcite, and CaO concentrations (Appendices B3 and B7; fig.13). When this high value sample is included in the data set, the correlations between Se and calcite and between Se and CaO appear to be significant (fig. 13). Upon removal of the data point with high Se, calcite, and CaO, and given that most of the samples have calcite concentrations that are below the limit of detection, there is no significant correlation between Se and calcite or CaO in USGS 11-10-ft (fig. 13).

For samples from USGS 12-10-ft, Se is significantly correlated with clay minerals (chlorite, kaolinite, and illite), calcite, and K_2O (fig. 14). The correlation between Se and chlorite is weak as there are many points without detectable Se or measurable amounts of chlorite, and the remainder of the points are distributed above and below the trend line. The correlations between Se and kaolinite, illite, calcite, and K_2O are also weak and thus the concentration of these minerals or K_2O is not a good predictor of the Se concentration.

Sulfur, Loss on Ignition, and Selenium in Roof, Parting, and Floor Samples

The data for coal-bed roof, parting, and floor samples from USGS 9 (Appendix B9) were analyzed to determine if there is a significant correlation between Se and total sulfur. The Se concentration has a range from below detection to 3340 μg/kg and total sulfur has a range of 0.01 – 2.22 percent for 26 samples. The results indicate that Se concentrations in the selected roof, parting and floor samples do not statistically correlate with total sulfur concentrations (a proxy for the mineral pyrite, FeS_2) (fig. 15). Therefore, it is unlikely that a significant portion of Se is associated with pyrite in these samples.

The data for coal-bed roof, parting, and floor samples from USGS 9 were also analyzed to determine if there is a significant correlation between Se and organic matter. The loss on ignition data, calculated from ash analyses, were used as a proxy for the amount of organic matter. The range of loss on ignition is 6 – 48 percent (Appendix B9). Statistical evaluation of the data indicate that the Se concentrations in the roof, parting, and floor samples are correlated with the loss on ignition at the 5 percent level of significance (R = 0.480, which exceeds the critical value for $R_{(0.05)} =$ 0.388) (fig. 16). The positive correlation between Se and loss on ignition suggests that Se may occur as organically bound Se.

The statistical comparisons conducted in the present study do not provide an unequivocal indication of any relation between Se concentrations and sample mineralogy or sample chemistry. The positive correlations that were noted between Se concentrations and sample mineralogy cannot be applied with certainty on the basis of the data derived in the present study. Therefore, further investigation is needed to determine the mode of occurrence of Se in coal-bearing strata and its association with both inorganic and organic material.

Aqueous Extraction of Soluble Selenium

There is no generally accepted standard method for the determination of soluble Se in rock samples. Therefore, in order to estimate soluble Se in the present study, both the saturated paste

extract (SPE) and sequential water extraction (SWE) methods described above were used to evaluate the amount of Se extracted by water.

The concentration of Se extracted into water from rock, was compared to the total amount of Se in the rock. The Se concentration (μg/L or ppb) extracted from rock samples by the SPE method was compared to the total Se concentration (μg/kg or ppb) in rock samples from USGS 9-10-ft (fig. 17), USGS 11-10-ft (fig. 18), and USGS 12-10-ft (fig. 19). The Se concentration (μg/L) extracted from rock samples by the SWE method also was compared to the total Se concentration (μg/kg) in rock samples from USGS 11-10-ft (fig. 20). In several rock samples, the Se concentration is below the detection limit of the GFAA method, yet detectable concentrations of Se are leached by SPE or SWE methods. In other cases, high concentrations of Se are measured in rock samples yet low concentrations of Se are leached from the rock (figs. 17, 18, 19, 20). Se concentrations in SPE leachates from rock do not correlate with Se concentration in the rock in any of the three cores (figs. 17, 18, and 19). Furthermore, the Se concentration in leachates from either the SPE or the SWE leaching method do not correlate with the Se concentration in the rock in core USGS 11 (figs. 18 and 20).

The reproducibility of water extraction of soluble Se from freshly ground rock samples was examined in core USGS 11. Comparison of Se concentration in leachates of duplicate sub-samples, SWE-A and SWE-B, give consistent results (fig. 21). It is not clear why Se concentrations are higher in SWE-B than in SWE-A in 13 of 15 samples leached in duplicate (Appendix B13). In the SWE extractions, two times as much mass of water (10 ml) as rock (5 g) was used and each sub-sample was processed in the same way. The correlation coefficient is high with an R = 0.9709 for 15 samples (fig. 21). Although SWE leaching is not a standard method to determine soluble Se, it appears to give reliable results, and the scatter of data points suggests that soluble Se concentrations appear to be reproducible within a factor of two.

The two methods of extracting soluble Se from rock were compared to determine whether the water to rock mass ratio used in the extraction influences either the concentration of Se in the water-extract leachate or the amount of Se extracted from the rock. The SPE method used 0.011 L water / 0.030 kg rock whereas the SWE method used 0.010 L water / 0.005 kg rock. Thus the SWE leach method used 5.4 times more water per kg of rock than the SPE method. The SPE-A and the SWE-A extractions, both first extraction leachates, were conducted on 44 duplicate rock samples from USGS 11-10-ft. Two observations were made. First, the concentration of Se is higher in SPE-A leachates than in SWE-A leachates in 38 of 44 samples (fig. 22) with a high correlation coefficient R = 0.8340 that suggests each method gives internally consistent results. The lower Se concentrations in SWE-A leachates compared to SPE-A leachates may be a result of dilution by more water used per mass of rock leached in the SWE method compared to the SPE method.

Second, in order to compare the amount of Se leached from rock by the two methods, the Se concentrations in SPE-A and SWE-A were normalized to account for the mass of water and rock used and is hereafter referred to as "absolute Se" with units of μg Se in solution / kg of rock leached. For SPE, the absolute Se is calculated by multiplying the Se concentration in leachate (μg Se / kg leachate) by 0.011 kg leachate / 0.030 kg rock and for SWE the absolute Se is calculated by multiplying the Se concentration in leachate (μg Se / kg leachate) by 0.010 kg leachate / 0.005 kg rock. Comparison of the absolute Se determined for the SWE and SPE methods for USGS 11 shows that the absolute Se extracted by SWE method is greater than the absolute Se extracted by the SPE method in 33 of 44 samples (fig. 23). The slope of the line in figure 23 indicates that the

SWE method extracts twice as much Se from rock as the SPE method. This suggests that the more water that comes in contact with rock, the more Se may be leached from the rock.

Sequential water extractions of Se by the SWE method were conducted in this study to determine whether the concentration of Se in leachates changes over time as successive amounts of water come into contact with the rock (Appendix B13; fig. 24). The results show that in cases where the initial leachate Se concentrations are high, approximately 30 μg/L or higher, there is a generally rapid decrease in Se concentrations in successive leachates. After several leaches, approximately four, the concentration of Se is lower, generally less than 15 μg/L, and fairly constant (fig. 24).

Discussion

Selenium Concentration, Lithology, and Mineralogy

The average Se concentrations in dominant rock types (lithologies) in this study were compared with the average Se concentrations in upper continental crust (Wedepohl, 1995; Rudnick and Gao, 2003) and sedimentary rocks (Horn and Adams, 1966; Baedecker and others, 1998). The average Se concentration in upper continental crust is estimated as 0.083 ppm by Wedepohl (1995) and 0.09 ppm by Rudnick and Gao (2003). However, sedimentary rocks only represent a small portion, approximately 14 percent, of the upper continental crust (Wedepohl, 1995). Horn and Adams (1966) estimated Se concentrations in six sedimentary and marine domains, including shale and sandstone, based on iterative geochemical mass balance calculations, starting with a range of Se concentrations reported in the literature. Se could not be brought into an internally consistent mass balance in the model, probably as a result of significant volcanic input, and should be considered as an order of magnitude estimate (Horn and Adams, 1966). The range and calculated average Se concentrations for shale and sandstone reported by Horn and Adams (1966) are similar to those for the central Appalachian basin shale and sandstone samples analyzed in this study (table 11). Se concentrations in shale, siltstone, and sandstone samples from the western U.S. are reported in the PLUTO data base (Baedecker and others, 1998). Average Se concentrations calculated for these western U.S. samples are approximately 5 to 7 times the average Se concentrations in shale, siltstone, and sandstone in the central Appalachian basin samples in this study (table 11). These comparisons suggest that the Se concentrations in central Appalachian sedimentary rocks associated with coal beds are not anomalously high when compared to upper continental crust, global estimated average sedimentary rocks, or western U.S sedimentary rocks.

Several recent studies have examined Se concentrations in various lithologies collected from cores drilled in coal-bearing strata in southern West Virginia (Jenkins and Schaer, 2005; Mullennex, 2005; Roy, 2005; Vesper and Roy, 2006). Samples in those studies were collected from different stratigraphic intervals, selected using different criteria, and categorized into different lithologic groups compared to this report. Also, data were presented with different emphases than in this report, for example, contrasting samples that were located close to or far from coal beds using either 5 ft (Mullennex, 2005) or 2 ft (Vesper and Roy, 2006) as the operational cutoff distance. Nevertheless, some general comparisons can be made to data presented in this report. Mullennex (2005) sampled 5 cores in one mine in southwestern West Virginia in the stratigraphic interval from the No. 6 Block coal, lower Allegheny Formation, down to the Coalburg coal, upper Kamawha Formation. This interval partially overlaps the upper part of the "upper stratigraphic interval" in this report. Mullennex (2005) presents mean Se concentrations for all shale and all

sandstone, regardless of proximity to coal beds. The mean Se concentrations for all shale and all sandstone in USGS 9-10-ft, USGS 11-10-ft, and USGS 12-10-ft core samples (table 11) are within a factor of three of those found by Mullennex (2005). Given the differences in sampling protocol and stratigraphic interval of Mullennex (2005) and this report, these results are fairly similar.

The present study evaluated Se concentrations in four rock types (claystone, shale, siltstone, and sandstone) in one core, USGS 9, to determine relations, if any, among rock-type and Se concentrations. For both USGS 9-LITH and USGS 9-10-ft samples, mean Se concentrations were equal in shale and claystone whereas mean Se concentrations in siltstone were greater than claystone (table 7). Other comparisons of mean Se concentrations among the lithologies were inconsistent from USGS 9-LITH samples to USGS 9-10-ft samples (table 7).

Mineralogy was determined by X-ray diffraction on all samples in four core sample sets. In one core, a correlation was found between siderite and Se whereas in another core, clay minerals (chlorite, kaolinite, and illite) correlated with Se. Calcite is below detection in most of the samples. In the few samples where calcite is present at high concentrations, the data suggest it may be associated with high Se content. There is no correlation between Se and any mineral that holds for all cores. Thus, if statistically significant correlations between Se concentrations and mineralogy exist, they are below the level of detection by the combined sampling, analytical, and statistical methods used in the present study.

Comparison of Se Concentration in Roof, Parting, Floor, and Four Dominant Lithologies

Coal-bed roof, parting, and floor samples from core USGS 9 were evaluated to determine the relation, if any, between these organic-rich samples that are adjacent to coal beds and their Se concentrations. The equality of the mean values and variances for each type of sample were used in the comparison. The variances and means are statistically equal among Se concentration for roof, parting, and floor samples as shown in table 8.

Collectively RPF (roof, parting, and floor) samples have mean Se concentrations equal to siltstone and greater than claystone and sandstone in core USGS 9 (figs. 10, 11; table 10). Another way of stating this is that organic-rich RPF samples located adjacent to coal beds have higher Se concentrations than sandstone samples with a distance from coal beds unspecified, for one core analysed. Jenkins and Schaer (2005) sampled 7 cores from 3 areas in southern West Virginia in the stratigraphic interval from the No. 5 Block coal, lower Allegheny Formation, to the Winifrede coal, upper Kanawha Formation. They found higher concentrations of Se in dark organic-rich rock close to coal beds compared to sandstone farther from coal beds. Roy (2005) and Vesper and Roy (2006) examined one core in the Coalburg through the Winifrede interval in the upper Kanawha Formation. Vesper and Roy (2006) and Mullennex (2005) found a trend of more Se in organic-rich rock ('carbolith' or 'coal and shale') than shale than sandstone. The rank order for mean Se concentration for USGS 9-LITH was RPF (organic-rich rock close to coal) > sandstone > shale and for USGS 9-10-ft RPF > sandstone = shale (tables 7, 10). The difference in the rank order of the mean Se concentration of various lithologies (organic-rich rock, shale, and sandstone) compared between results found in this report and those published in the literature may be a result of different sampling protocols and different stratigraphic intervals examined.

In this report, the Se concentrations in RPF samples do not correlate with sulfur (a proxy for pyrite) but do correlate with loss on ignition (a proxy for organic matter). Similarly, Mullennex

(2005) found no correlation between Se and total, pyritic, or organic sulfur in samples from the No. 6 Block coal bed through the Coalburg coal bed stratigraphic interval. Roy (2005) and Vesper and Roy (2006) did not find any strong correlation between Se and sulfur content or organic matter in rock samples.

Mobilization of Soluble Selenium

The results of the saturated paste extract (SPE) and sequential water extraction (SWE) studies reported herein should be used with caution because standard leaching methods have not been developed, nor have definitive Se laboratory leaching studies been conducted. The SPE results of this study suggest that total Se in rock is not a predictor for soluble Se. Roy (2005) and Vesper and Roy (2006) also noted that soluble Se was not correlated to total Se in rock. SPE or some other leaching procedure, rather than total Se values determined on whole-rock samples, may provide a more accurate indication of the potential for Se mobilization to streams following land disturbance.

The sequential water extraction (SWE) leaching method used in this study gives results that appear to be reproducible within a factor of approximately two (Appendix B13; fig. 21). Given the potential for differences in particle sizes, mineralogy, and modes of occurrence of Se in the duplicate sub-samples, this reproducibility is fairly good.

Comparison of the two leaching methods (SPE and SWE) used in this study suggest that the more water that comes into contact with rock, such as groundwater flow through rock, (1) the lower the concentration of resultant dissolved Se and (2) the more Se will be leached from the rock. In disturbed strata, the surface area of rock exposed per mass of rock is almost certainly less than in the < 60 mesh rock samples used for SPE and SWE leaching in this study. Therefore, one would expect less efficient leaching of Se in disturbed rock strata than in these laboratory studies.

The sequential leaching studies presented here suggest that Se concentrations of water passing through disturbed rock strata may have an initial increase in Se followed by a decrease in Se concentrations. Thus, soluble Se may be removed rapidly from disturbed rock strata with freshly exposed surfaces. Bonta and Dick (2003) observed an increase in Se concentration in streams below coal mining, at three of three mines studied during mining in the northern Appalachian basin in Ohio. They found that at one of two coal mines with data after mining, Se concentrations decreased to pre-mining levels within 6 years. The sequential leaching studies presented here indicate that the "half life" of dissolution of Se from coal-bearing lithologies may be relatively short; suggesting that the relative enrichment of Se in streams draining disturbed areas may decrease to baseline levels within a relatively few years.

Summary and Conclusions

The results and conclusions of the present study are summarized as follows:

- The precision of the analytical results for total Se in rock samples presented herein are consistent with the precision of the analytical method, ASTM 3052, that was used.

- The average Se concentrations in the four dominant lithologies in coal-bearing strata in the central Appalachian basin, as determined in the present study, are similar to the global average

Se concentrations reported for equivalent lithologies (Horn and Adams, 1966) and therefore are not anomalous.

- Rank order of the mean Se concentrations in all coal-bearing lithologies shows that mean Se concentrations are higher in upper strata (Stockton A coal bed to Chilton A coal bed) than in lower strata (Chilton A coal bed to Fire Clay coal bed) in three widely spaced cores in the central Appalachian basin in southern West Virginia. This stratigraphic trend is similar to the stratigraphic trend in Se concentrations in coal beds in the central Appalachian basin reported by Neuzil and others (2005).

- On the basis of data derived from analyses of samples obtained from three cores in this study, there is no demonstrable regional variation (trend) in Se concentrations.

- The present study evaluated Se concentrations in a variety of lithologies, rock types, to determine relations, if any, among rock-type and Se concentrations. The results indicate that average Se concentrations tend to be higher in siltstone compared to claystone, shale, and sandstone. When the means and variances of Se concentration are compared in claystone, shale, and sandstone, there are no statistically demonstrable differences. If differences exist, they are below the limits of verification by the methods used in the present study.

- Although Se concentrations correlate with some minerals (siderite, chlorite, kaolinite, and illite as determined by XRD) in some cores, Se does not consistently correlate with any mineral in all cores.

- Se concentrations were determined in selected coal-bed roof, parting, and floor samples from one core. When the data are evaluated statistically, taking into account the mean and variances, there are no demonstrable differences in mean Se concentrations among roof, parting, and floor samples.

- Se concentrations do not statistically correlate with total sulfur concentrations suggesting that there is not a correlation with pyrite in the selected coal-bed roof, parting, and floor samples. However, Se concentrations in the selected coal-bed roof, parting, and floor samples do correlate with the loss on ignition, which suggests an association of Se with organic matter. If so, rates of mobilization of Se from these organic-rich materials are expected to be controlled by relatively slow rates of chemical oxidation of the host organic matter. General principles of chemistry suggest that oxidation and dissolution of refractory organic compounds are typically quite slow at ambient conditions.

- The uncertainties associated with the analyses of low concentrations of Se in whole-rock samples and the lack of correlation between total Se in rock and susceptibility of Se to dissolution suggest that leaching tests, rather than whole-rock analyses, may provide a more useful estimation of the potential for Se dissolution and mobilization from coal-bearing strata and the potential for increased Se concentrations in surface streams as a result of land disturbances.

- The readily soluble fraction of total Se in coal-bearing strata is not known. However, the cursory study of sequential leaching conducted in the present investigation indicates that readily soluble Se may be rapidly removed from rock debris following disturbance of strata. It appears that the "half life" of dissolution is relatively short, suggesting that any relative enrichment of Se in streams draining disturbed areas may decrease to baseline levels within a relatively few years after disturbance. Substantiation of the conclusion that Se leaching from disturbed strata will have a short half life will require further testing at reclaimed sites.

On the basis of the present study, the average concentrations of Se in Middle Pennsylvanian coal-bearing strata in the central Appalachian basin are not anomalous when compared to published values of similar rock types. In addition, the average and spread (mean and dispersion) of Se concentrations indicate that if either stratigraphic or regional trends exist, such trends can not be verified statistically by the methods used herein. Also, there is no apparent association of Se with a specific rock type (claystone, shale, siltstone, or sandstone) with the possible exception of Se enrichment in certain siltstones. Leaching test methods, rather than total Se content of rocks, may more accurately represent the potential for Se mobilization by land disturbance.

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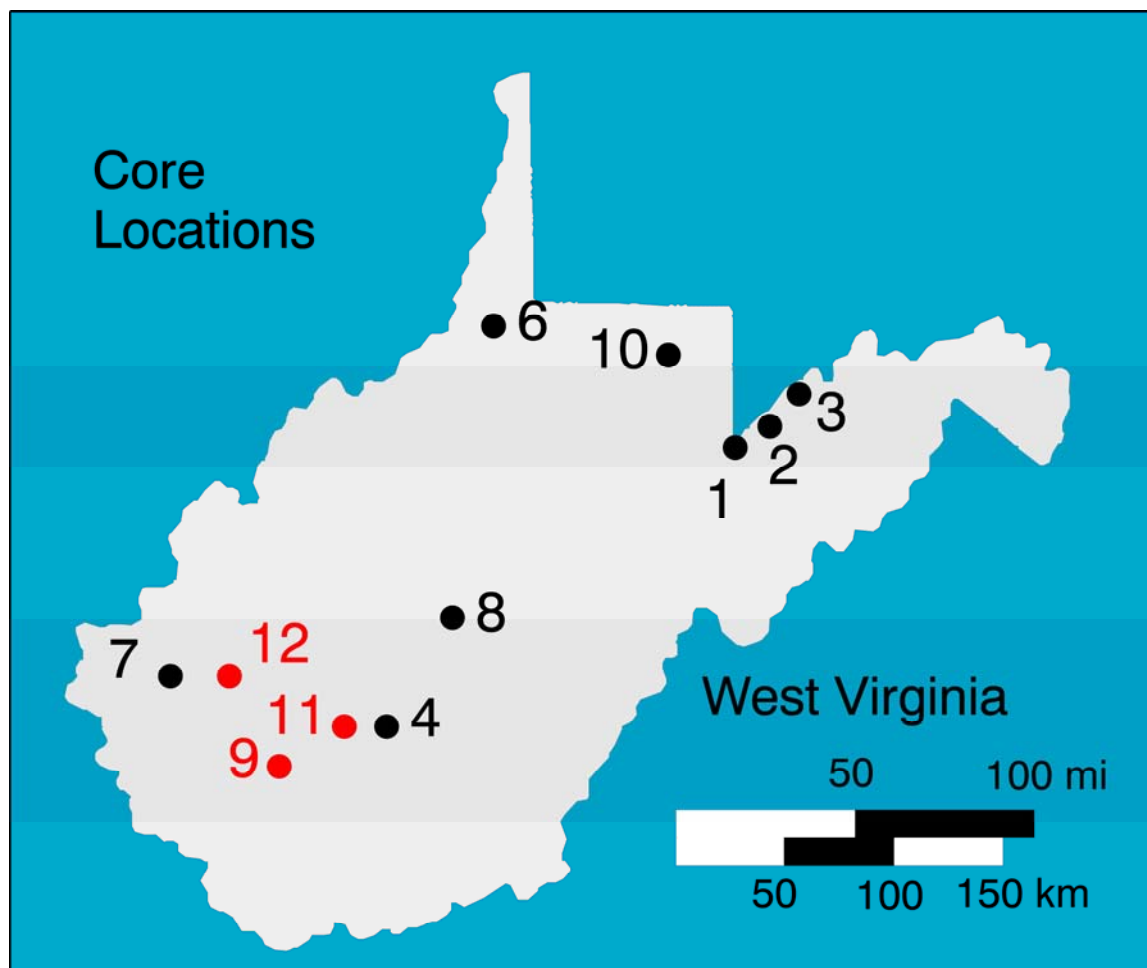
Figure 1. Map showing the location of three widely spaced cores (USGS 9, USGS 11, and USGS 12, indicated by red dots) in West Virginia, used in this study as part of a regional study of geochemical variation in the central Appalachian basin.
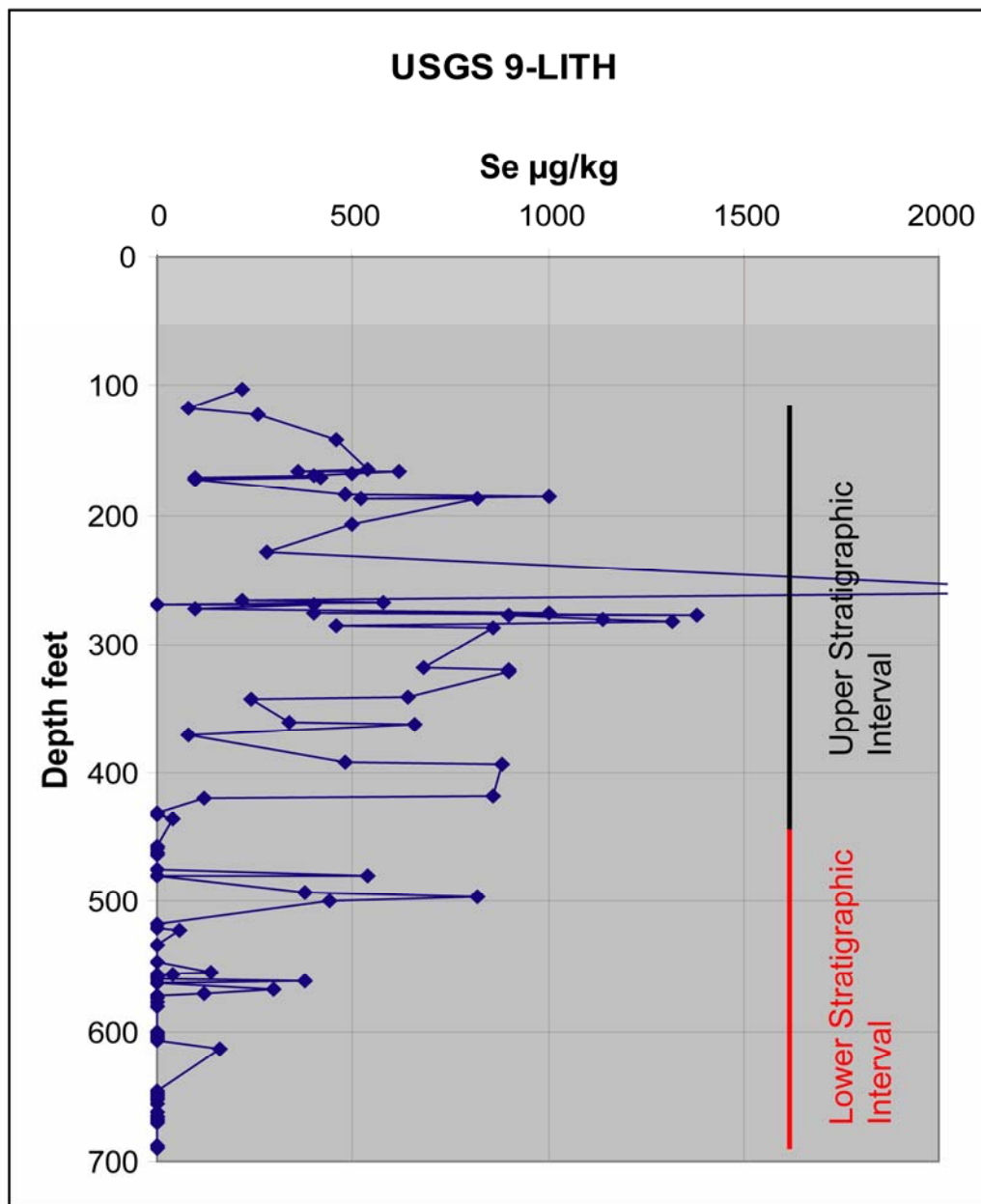
Figure 2. Se concentration (µg/kg) versus depth (ft) in core USGS 9-LITH samples, 1-foot increment samples selected by lithology.

The interval from the base of the Stockton A coal bed (114 feet) down to the top of the Chilton A coal bed (446 feet) is referred to as the upper stratigraphic interval. The interval from the base of the Chilton A coal bed (448 feet) down to the top of the Fire Clay coal bed (690 feet) is referred to as the lower stratigraphic interval. One Se value of 2440 µg/kg at 258-259 feet is larger than the maximum x-scale of 2000 µg/kg Se.

Data are from Appendix B1. [symbols indicate depth in core and Se concentration of rock samples analyzed; lines connecting symbols are for illustration purposes only and do not indicate Se concentrations of rock]
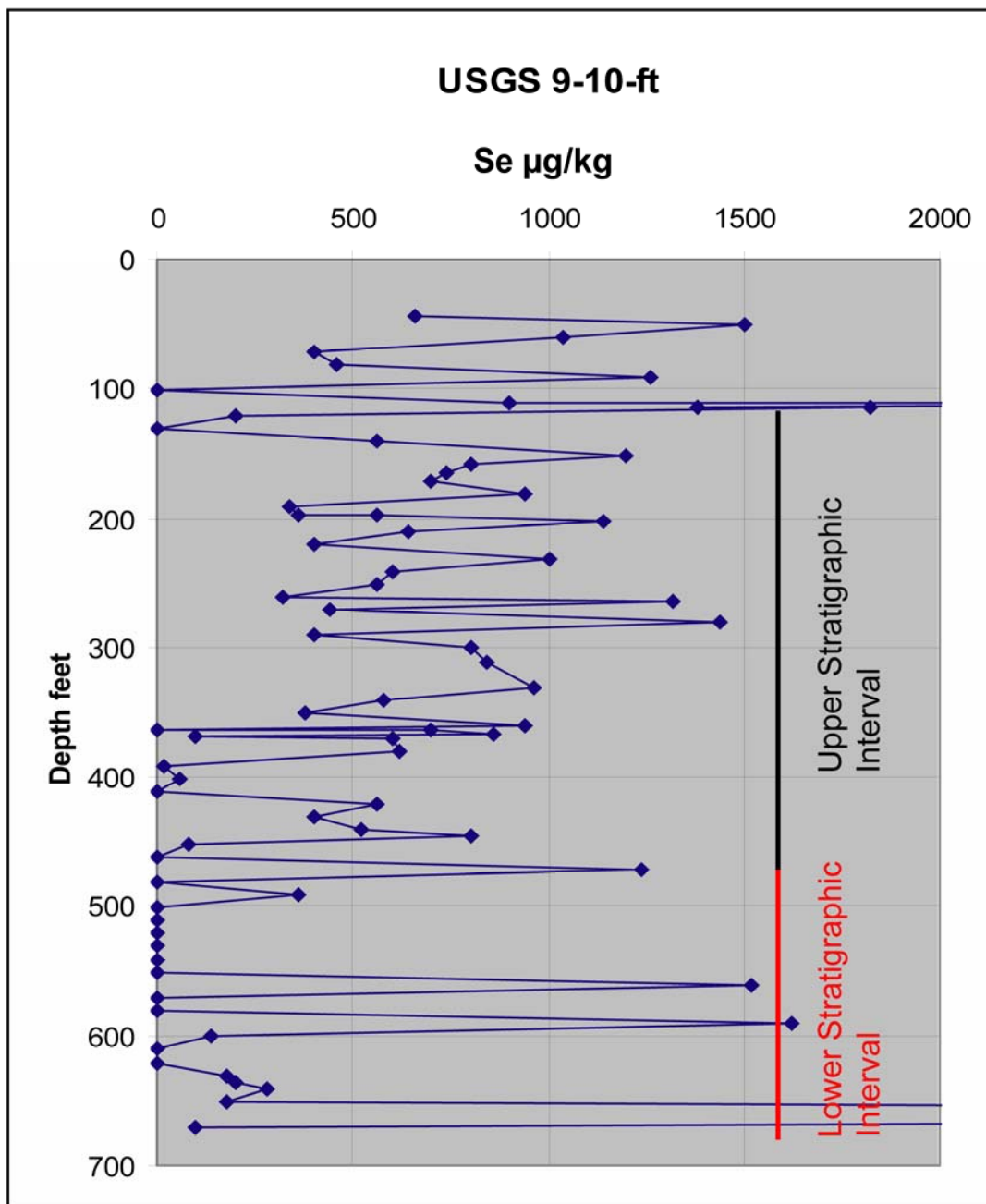
Figure 3. Se concentration (μg/kg) versus depth (ft) in core USGS 9-10-ft samples, 1-foot increment samples collected at 10-foot intervals.

The interval from the base of the Stockton A coal bed (114 feet) down to the top of the Chilton A coal bed (446 feet) is referred to as the upper stratigraphic interval. The interval from the base of the Chilton A coal bed (448 feet) down to the top of the Fire Clay coal bed (690 feet) is referred to as the lower stratigraphic interval. Two Se values of 3300 μg/kg at 110.42-110.90 feet, and 6820 μg/kg at 660-661 feet are larger than the maximum x-scale of 2000 μg/kg.

Data are from Appendix B2. [symbols indicate depth in core and Se concentration of rock samples analyzed; lines connecting symbols are for illustration purposes only and do not indicate Se concentrations of rock]
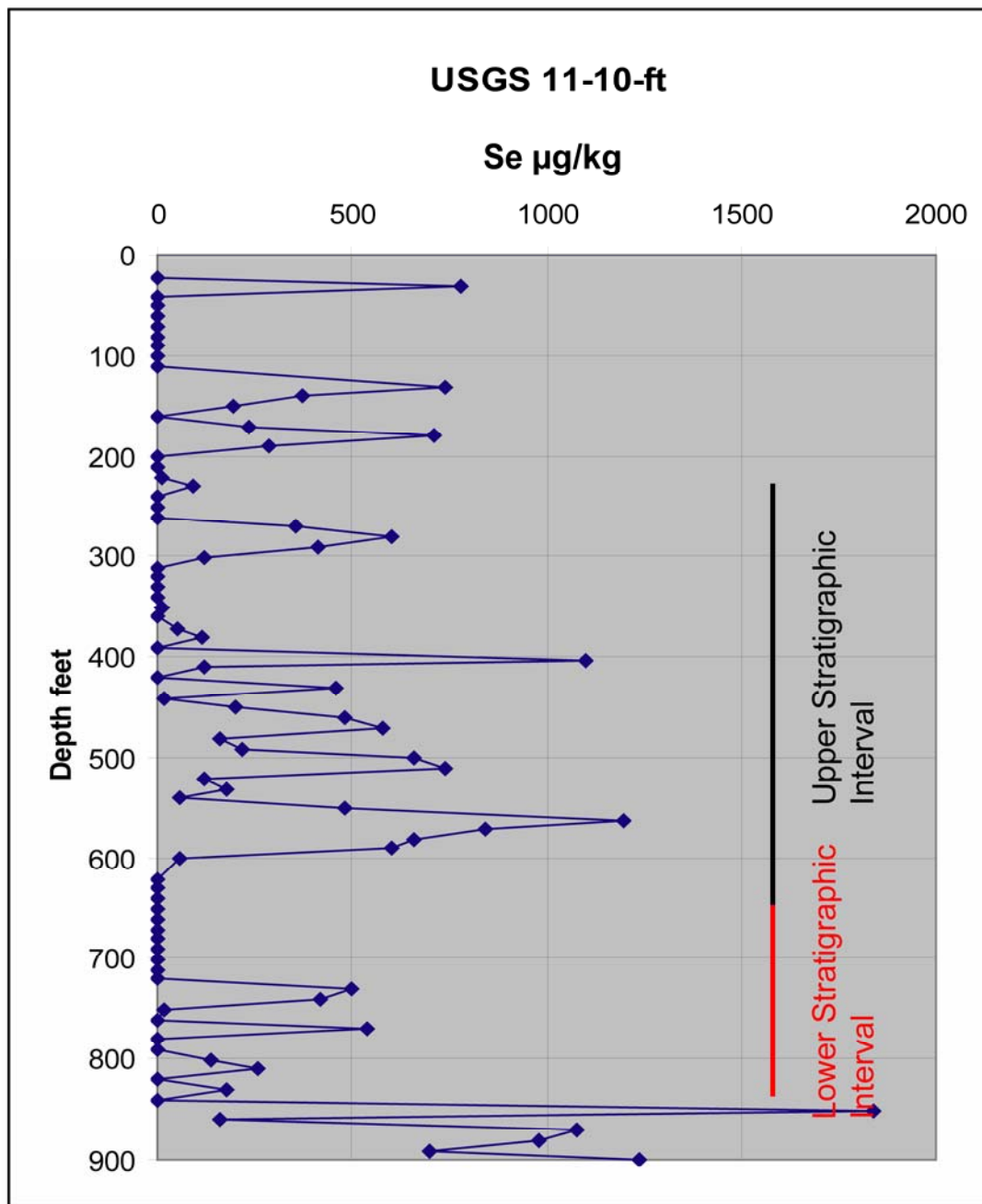
Figure 4. Se concentration (µg/kg) versus depth (ft) in core USGS 11-10-ft samples, 1-foot increment samples collected at 10-foot intervals.

The interval from the base of the Stockton A coal bed (239 feet) down to the top of the Chilton A coal bed (652 feet) is referred to as the upper stratigraphic interval. The interval from the base of the Chilton A coal bed (653 feet) down to the top of the Fire Clay coal bed (828 feet) is referred to as the lower stratigraphic interval.

Data are from Appendix B3. [symbols indicate depth in core and Se concentration of rock samples analyzed; lines connecting symbols are for illustration purposes only and do not indicate Se concentrations of rock]
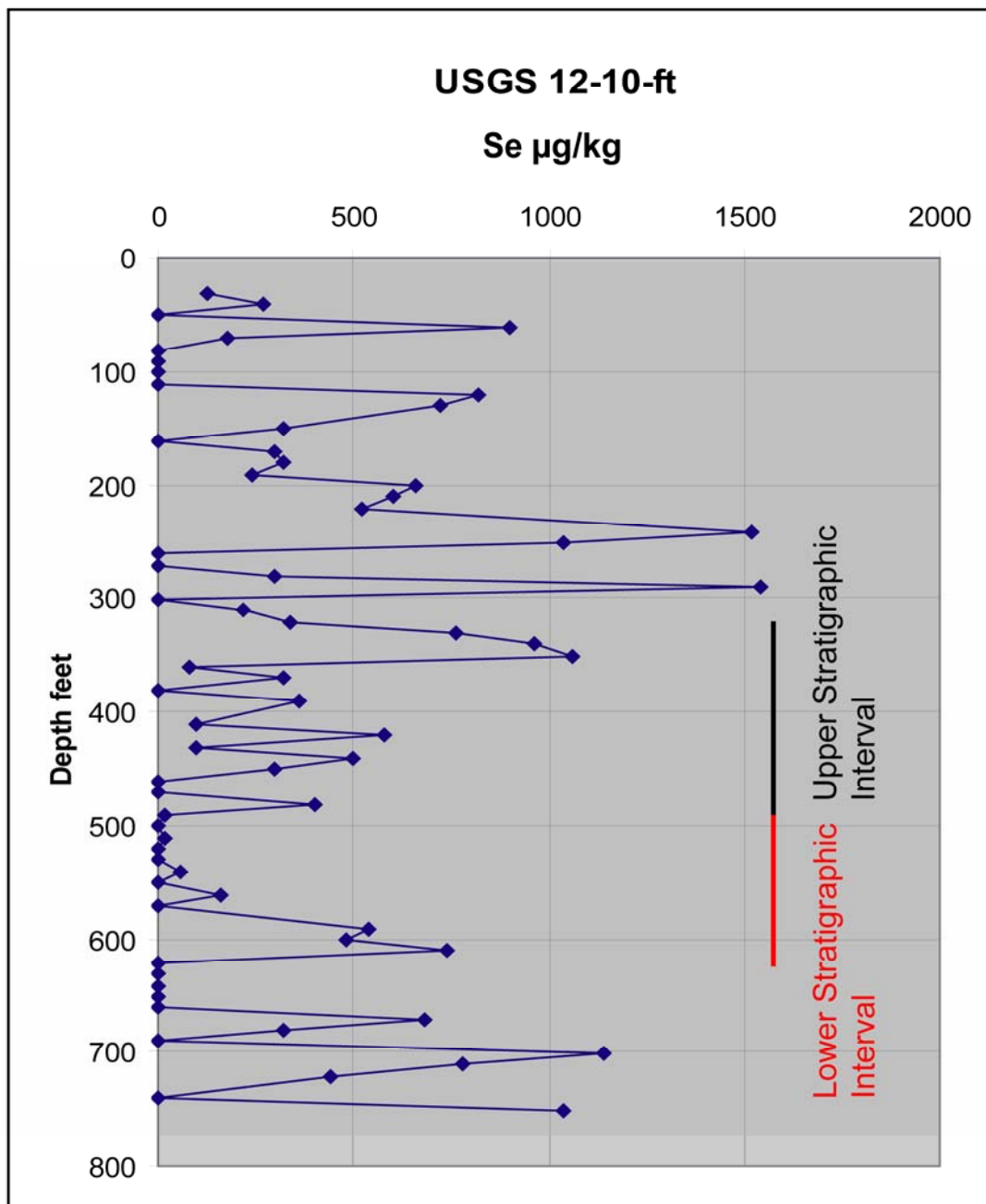
Figure 5. Se concentration (μg/kg) versus depth (ft) in core USGS 12-10-ft samples, 1-foot increment samples collected at 10-foot intervals.

The interval from the base of the Stockton A coal bed (316 feet) down to the top of the Chilton A coal bed (492 feet) is referred to as the upper stratigraphic interval. The interval from the base of the Chilton A coal bed (493 feet) down to the top of the Fire Clay coal bed (625 feet) is referred to as the lower stratigraphic interval.

Data are from Appendix B4. [symbols indicate depth in core and Se concentration of rock samples analyzed; lines connecting symbols are for illustration purposes only and do not indicate Se concentrations of rock]
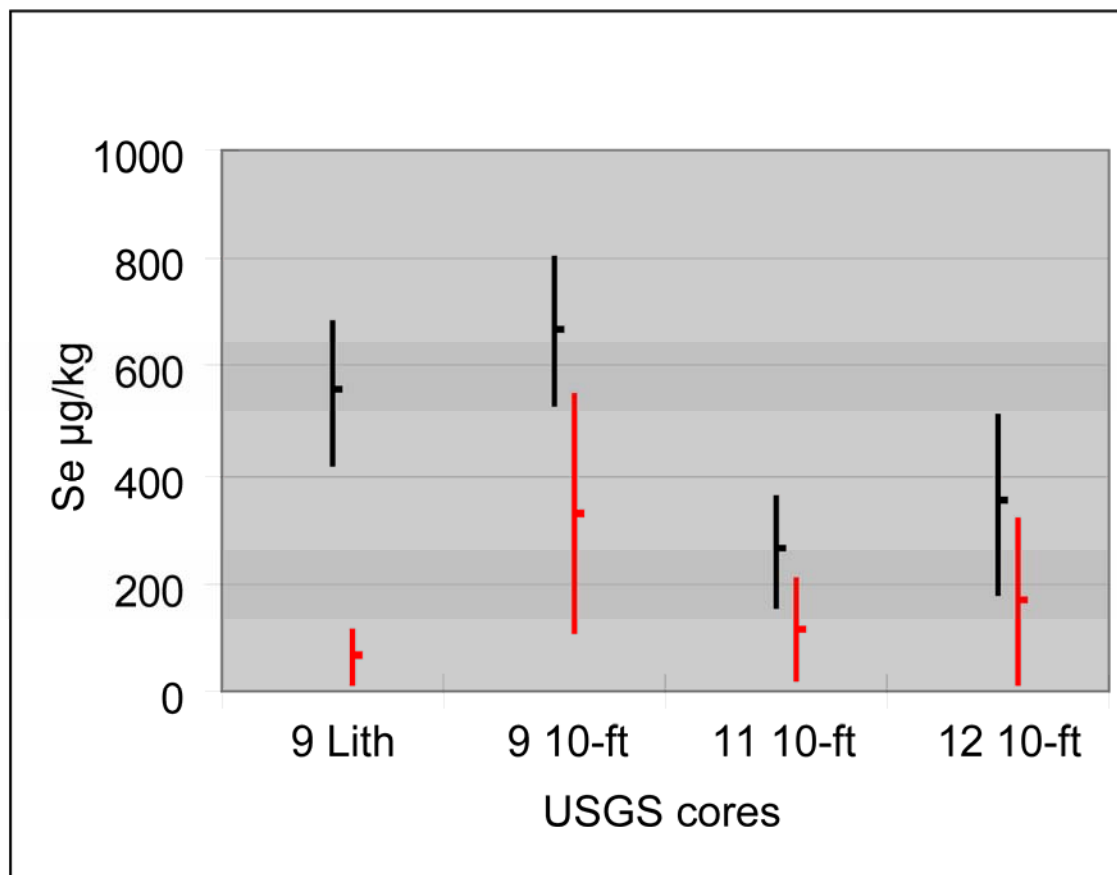
Figure 6. Mean Se concentration (µg/kg) ± 95 percent confidence interval (CI 95%) for upper and lower stratigraphic intervals in each core.

Data are from table 4. [upper stratigraphic interval (black), lower stratigraphic interval (red)]
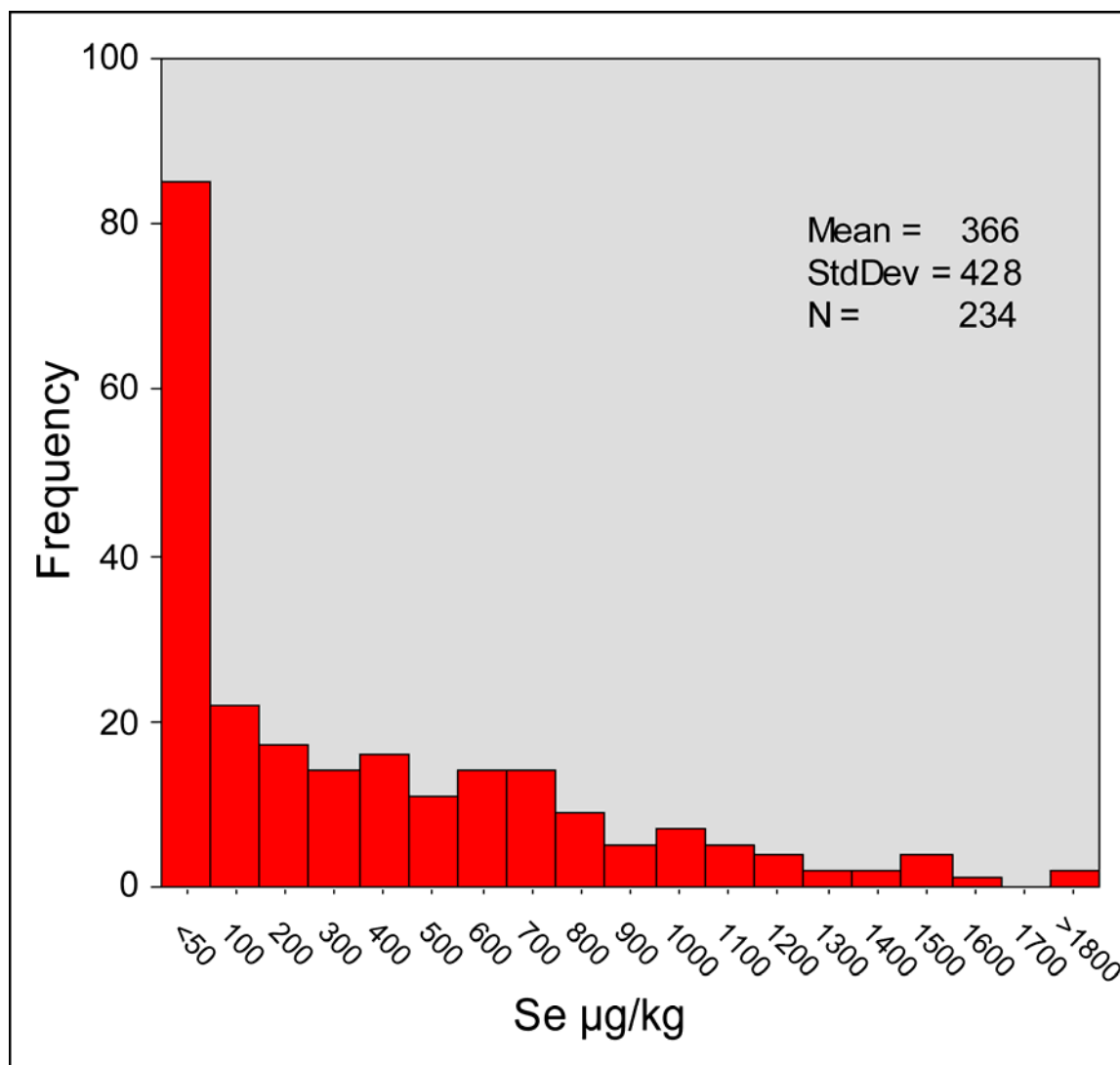
Figure 7. Frequency distribution of Se concentration (µg/kg) for all rock samples collected at 10-foot intervals from USGS 9-10-ft, USGS 11-10-ft, and USGS 12-10-ft.

Two high values for Se concentration (3300 and 6820 µg/kg in USGS 9-10-ft) are not included in mean and standard deviation calculations or shown on this figure. Bins are labeled by mid-point value, except for first bin (values <50) and last bin (values >1800).

Data are from Appendices B2, B3, and B4 and are summarized in table 6. [StdDev = standard deviation; N = number of samples]
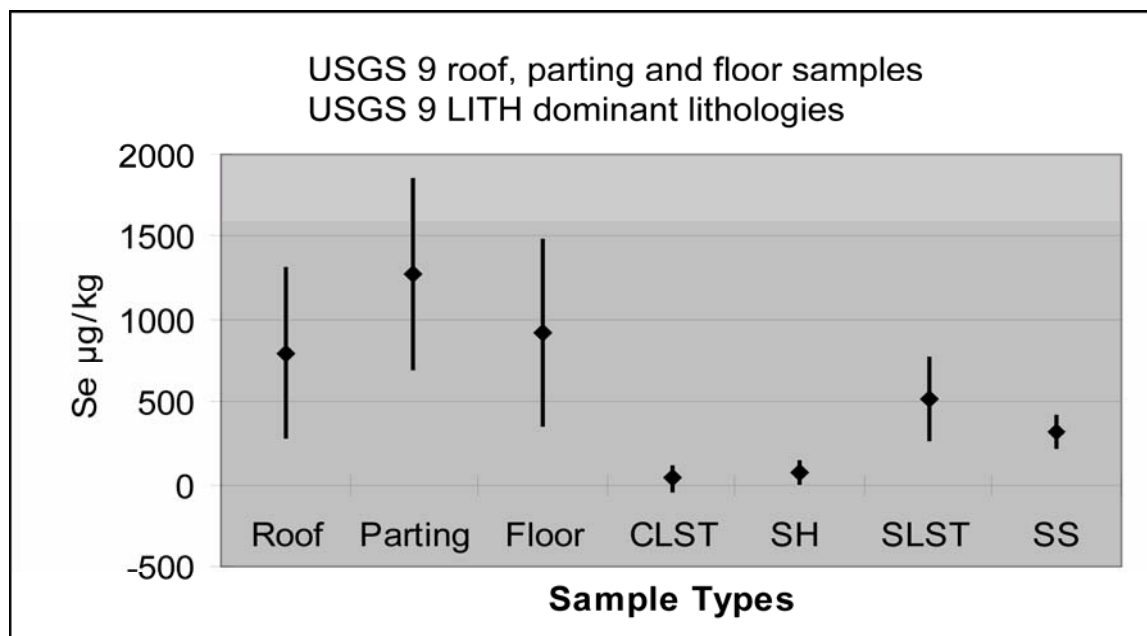
Figure 8. Mean Se concentration (μg/kg) ± 95 percent confidence interval (CI 95%) for four dominant lithologies from USGS 9-LITH and roof, parting, and floor samples from core USGS 9.

The rank-order of the mean Se concentrations for the seven sample types is: parting > floor > roof > siltstone > sandstone > shale > claystone.

Data are from tables 7 and 8. [CLST = claystone, SH = shale, SLST = siltstone, SS = sandstone]
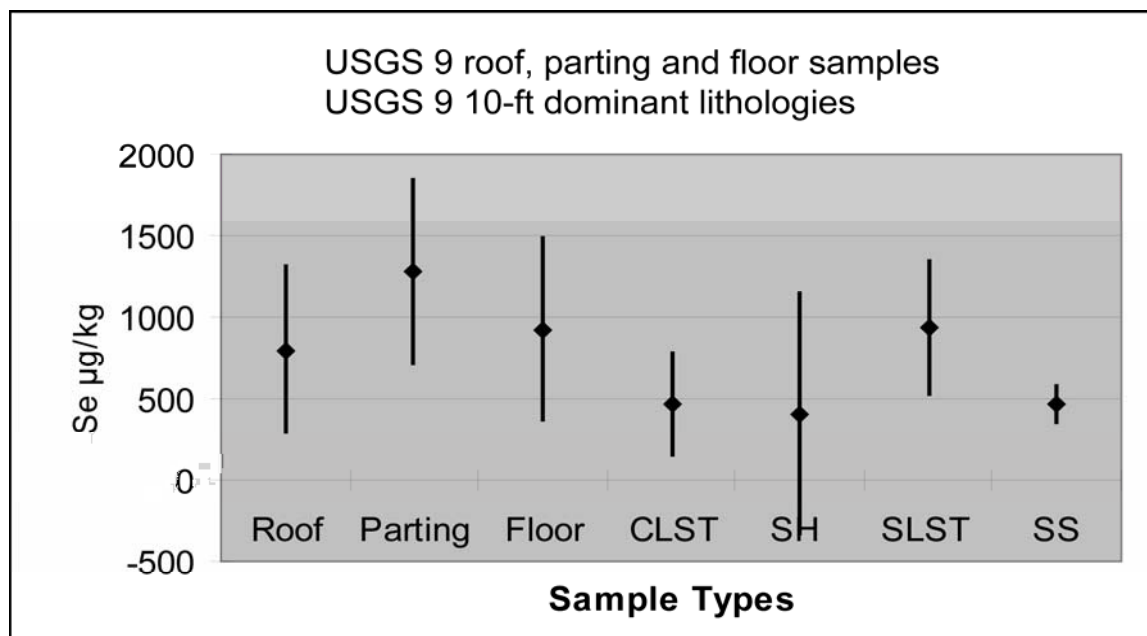
Figure 9. Mean Se concentration (µg/kg) ± 95 percent confidence interval (CI 95%) for four dominant lithologies from USGS 9-10-ft and roof, parting, and floor samples from core USGS 9.

The rank-order of the mean Se concentrations for the seven sample types is: parting > siltstone > floor > roof > sandstone > claystone > shale.

Data are from tables 7 and 8. [CLST = claystone, SH = shale, SLST = siltstone, SS = sandstone]
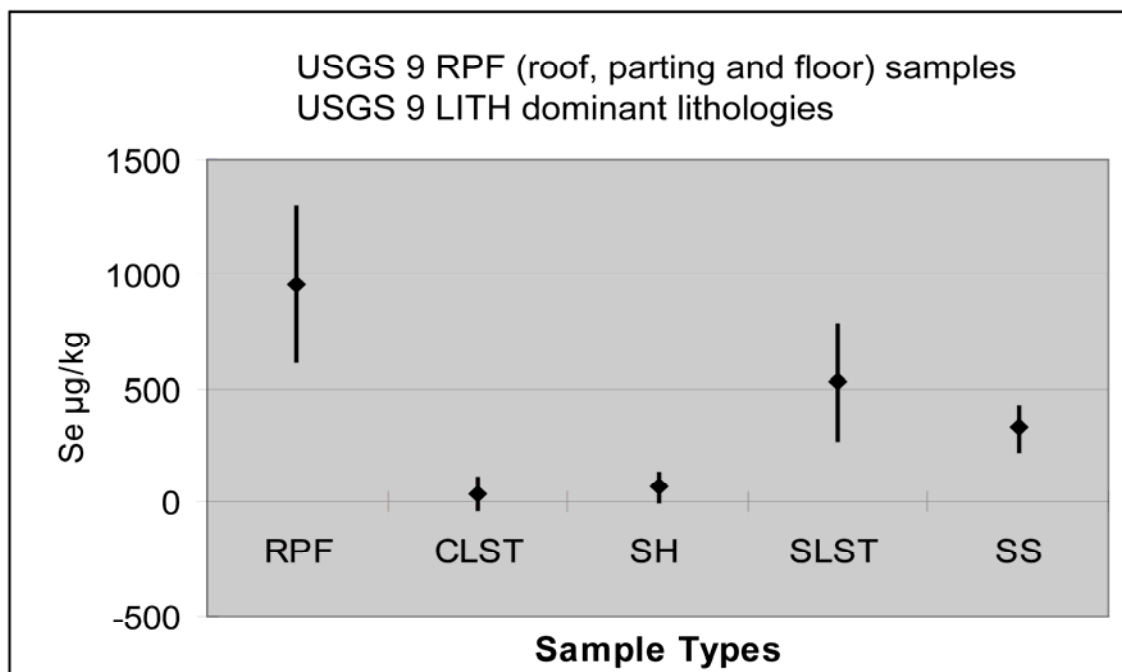
Figure 10. Mean Se concentration (µg/kg) ± 95 percent confidence interval (CI 95%) for four dominant lithologies from USGS 9-LITH and USGS 9-RPF (combined roof, parting, and floor samples from core USGS 9).

Statistical t-rests show that the mean Se concentration of RPF (952) is equal to the mean for siltstone (523) and greater than the means for claystone (33), shale (65), and sandstone (322).

Data are from tables 7, 9, and 10. [CLST = claystone, SH = shale, SLST = siltstone, SS = sandstone]
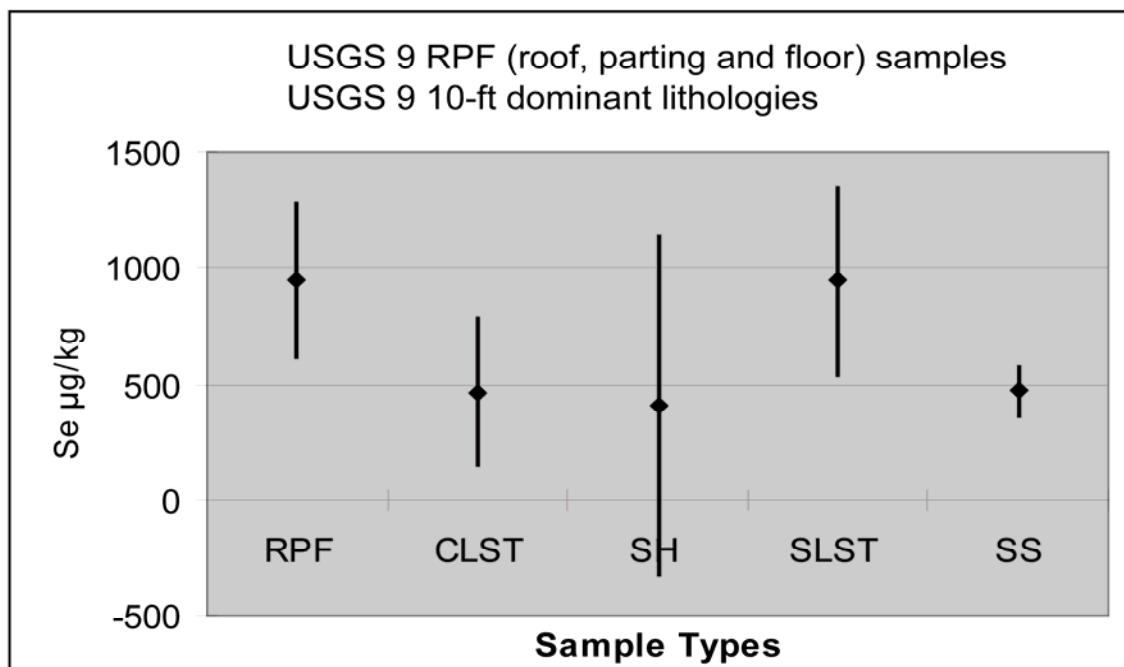
Figure 11. Mean Se concentration (μg/kg) ± 95 percent confidence interval (CI 95%) for four dominant lithologies from USGS 9-10-ft and USGS 9-RPF (combined roof, parting, and floor samples from core USGS 9).

Statistical t-tests show that the mean Se concentration of RPF (952) is equal to the means for shale (405) and siltstone (943) and greater than the means for claystone (464) and sandstone (467).

Data are from tables 7, 9, and 10. [CLST = claystone, SH = shale, SLST = siltstone, SS = sandstone]
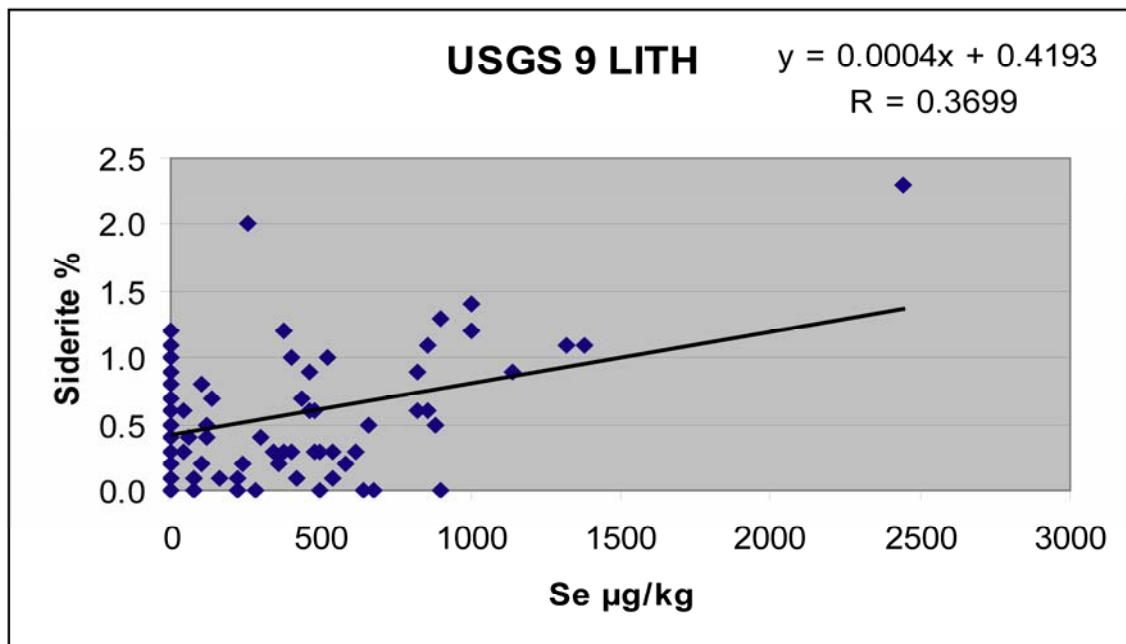
Figure 12. Se concentration (µg/kg) versus siderite (percent) in USGS 9-LITH.

Data are from Appendices B1 and B5.
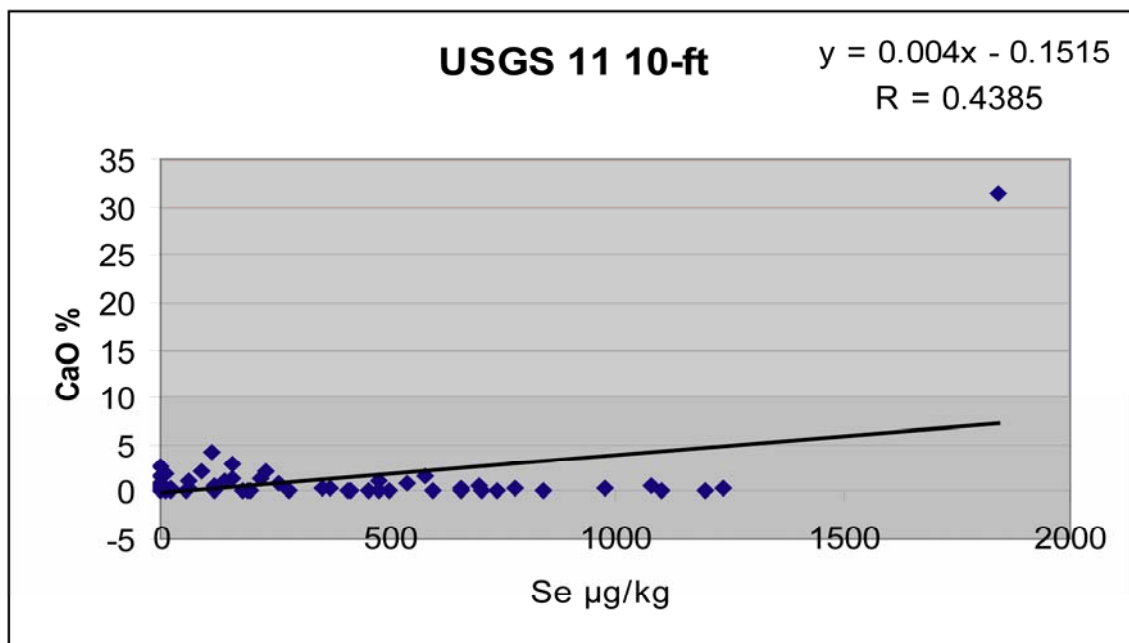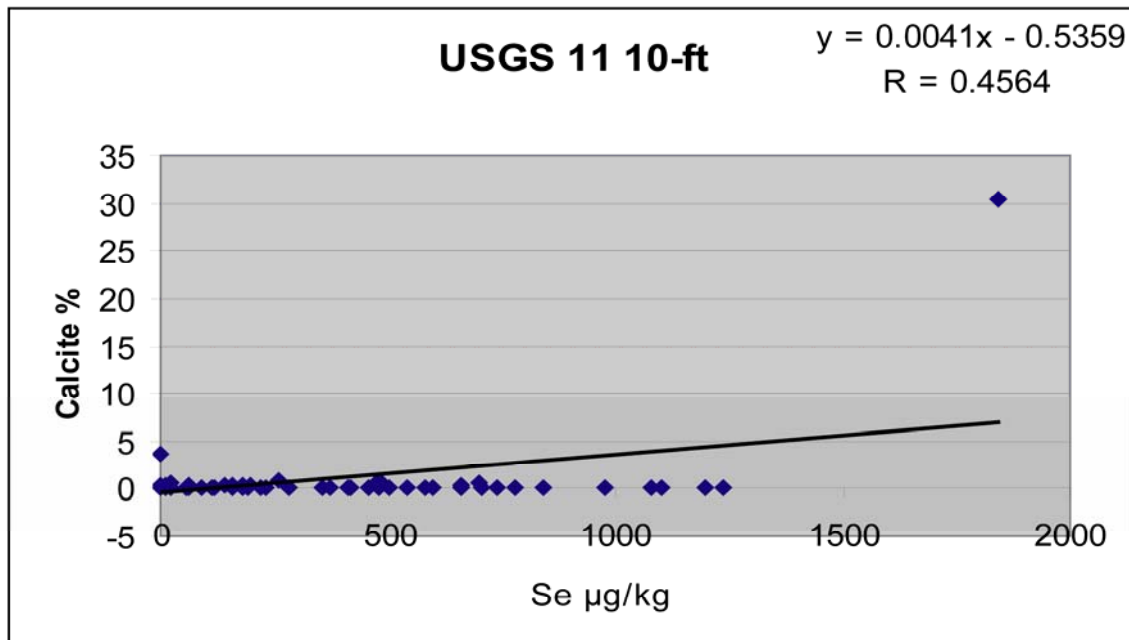
Figure 13. Se concentration (µg/kg) versus calcite and CaO (percent) in USGS 11-10-ft.

Upon removal of the point with high Se and high calcite the R value becomes 0.0762 and the correlation is no longer significant. Upon removal of the point with high Se and high CaO the R value becomes 0.10 and the correlation is no longer significant.

Data are from Appendices B3 and B7.
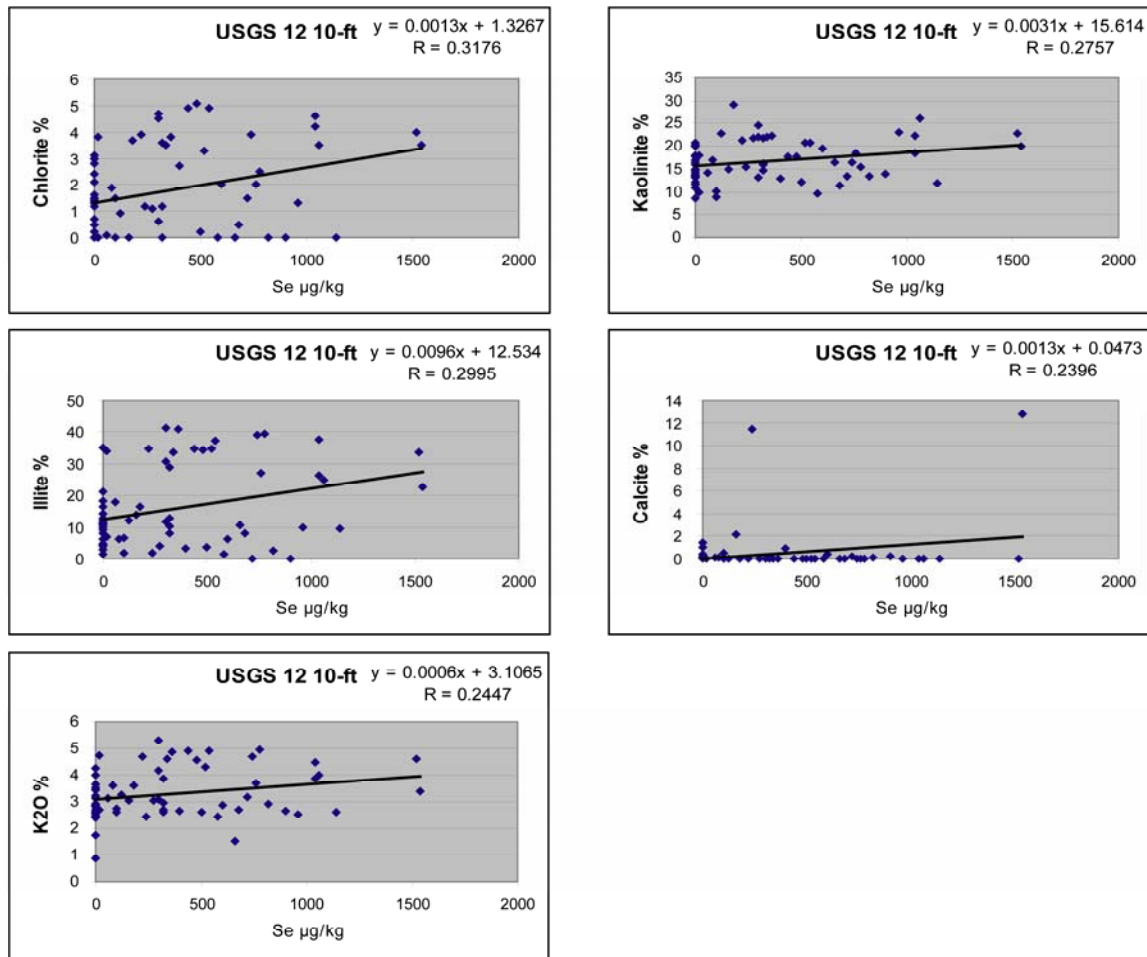
Figure 14. Se concentration (μg/kg) versus chlorite, kaolinite, illite, calcite, and K_2O (percent) in USGS 12-10-ft.

Data are from Appendices B4 and B8.
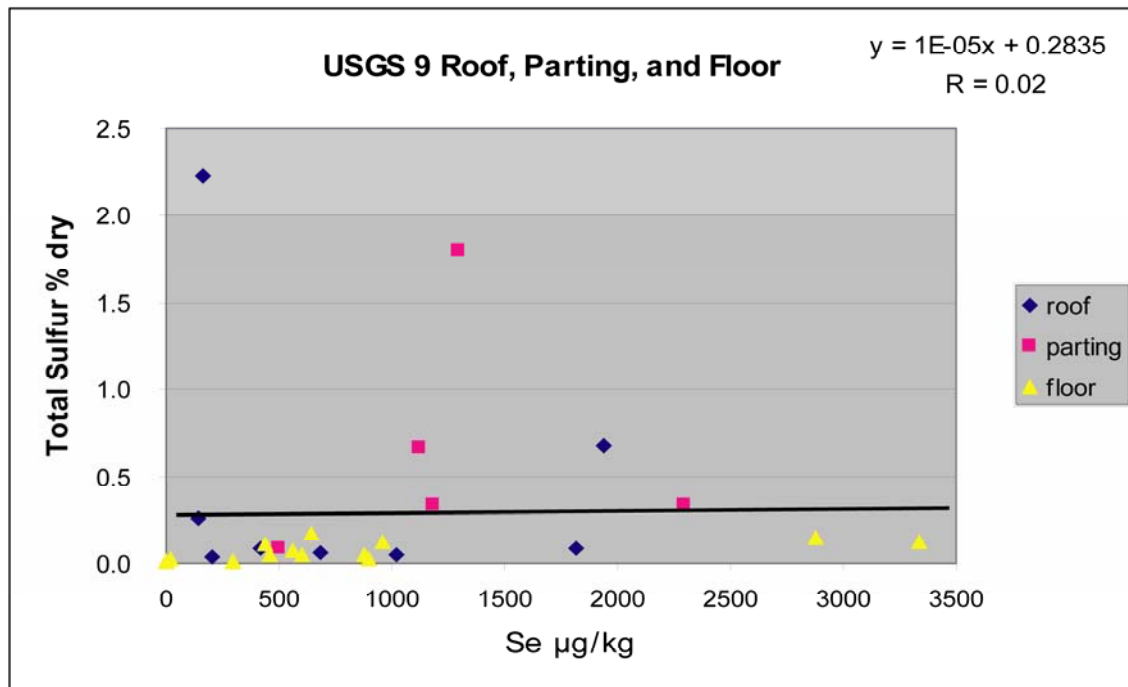
Figure 15. Se concentration (µg/kg) versus total sulfur (percent, dry basis) in roof, parting, and floor samples from USGS 9.

Data are from Appendix B9.
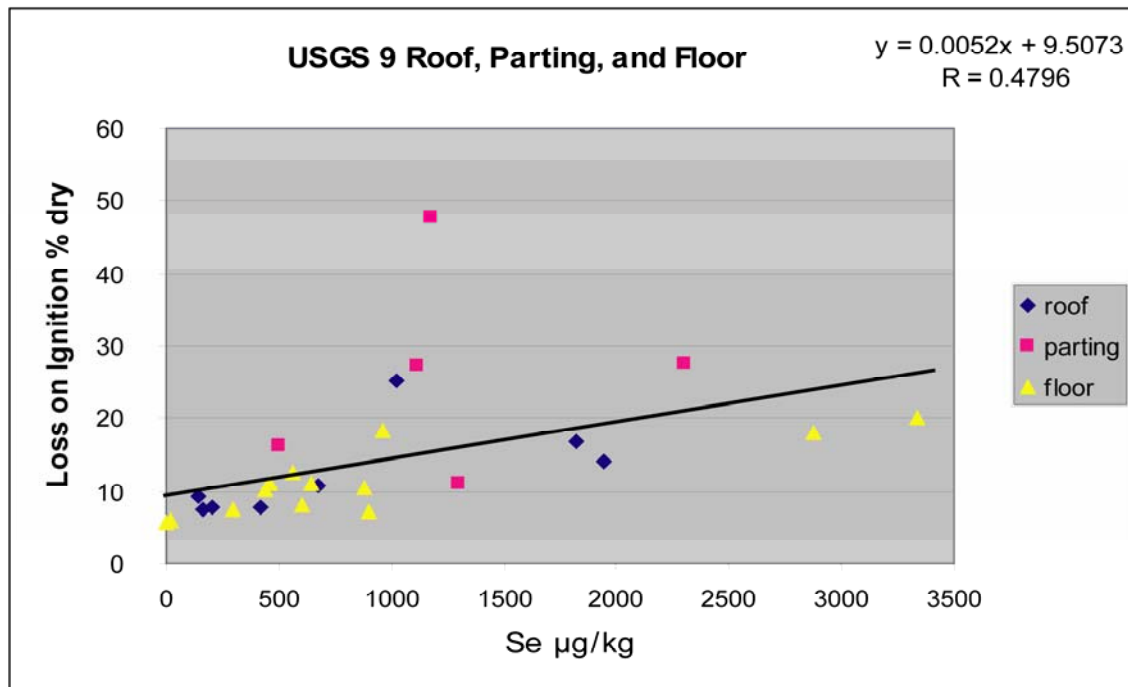
Figure 16. Se concentration (µg/kg) versus loss on ignition (percent, dry basis) in roof, parting, and floor samples from USGS 9.

Data are from Appendix B9.
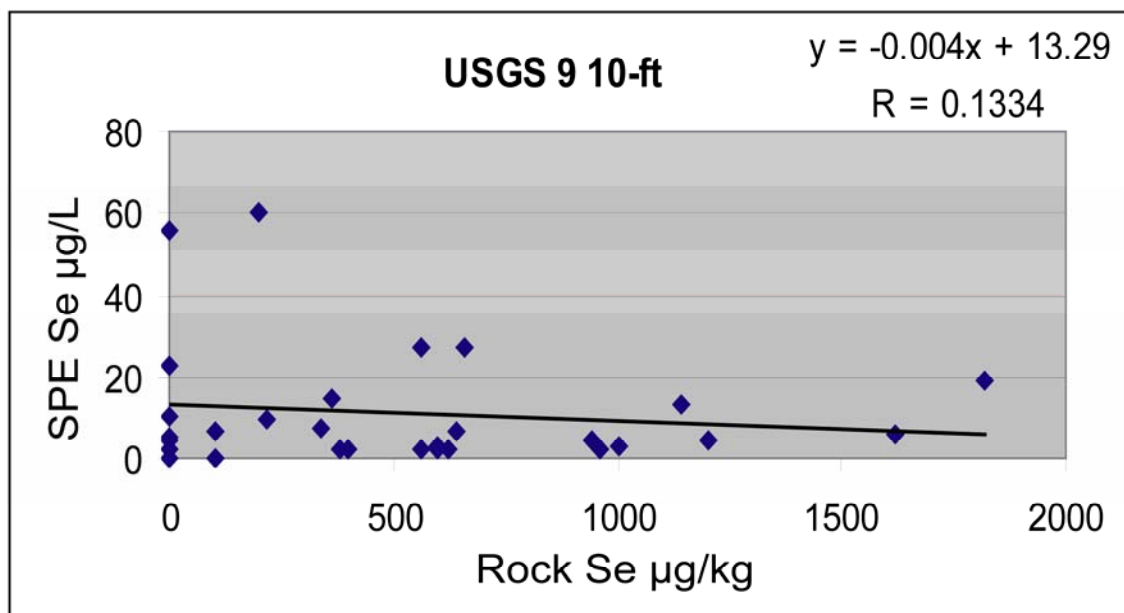
Figure 17. Se concentration (µg/L) in saturated paste extract (SPE) versus Se concentration (µg/kg) in rock samples from USGS 9-10-ft.

Two high Se values in rock (3300 and 6820 µg/kg) are not plotted and the correlation coefficient (R=0.1334) is not significant. If the two high Se values are included, the correlation coefficient is not significant either.

Data are from Appendices B2 and B10.
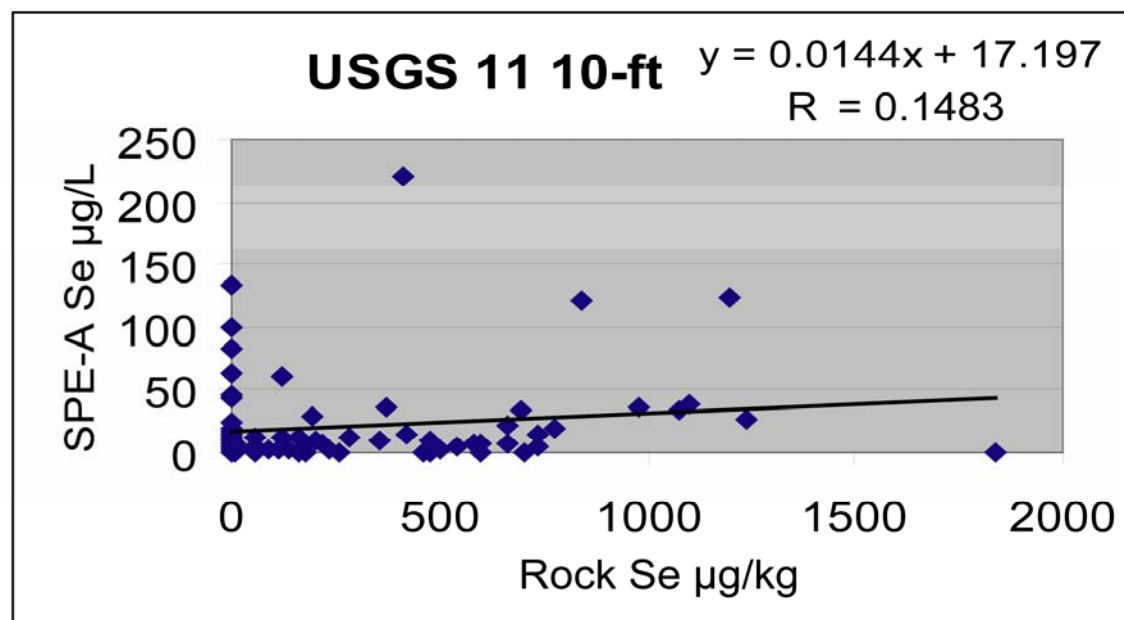
Figure 18. Se concentration (µg/L) in saturated paste extract (SPE-A) versus Se concentration (µg/kg) in rock samples from USGS 11-10-ft.

Data are from Appendices B3 and B11.
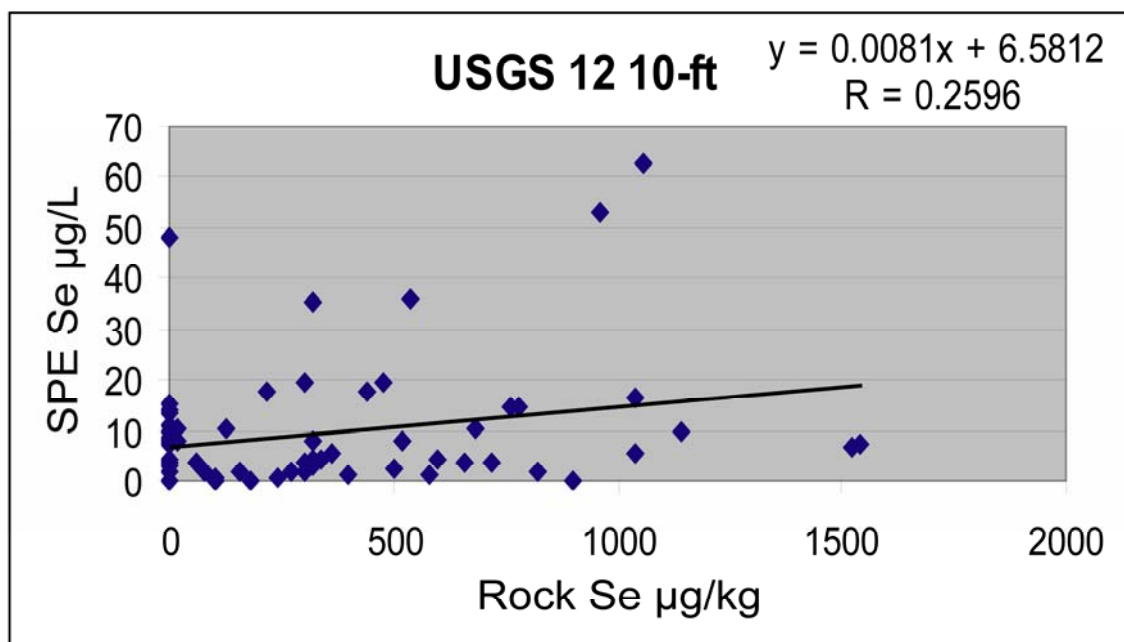
Figure 19. Se concentration (µg/L) in saturated paste extract (SPE) versus Se concentration (µg/kg) in rock samples from USGS 12-10-ft.

Data are from Appendices B4 and B12.
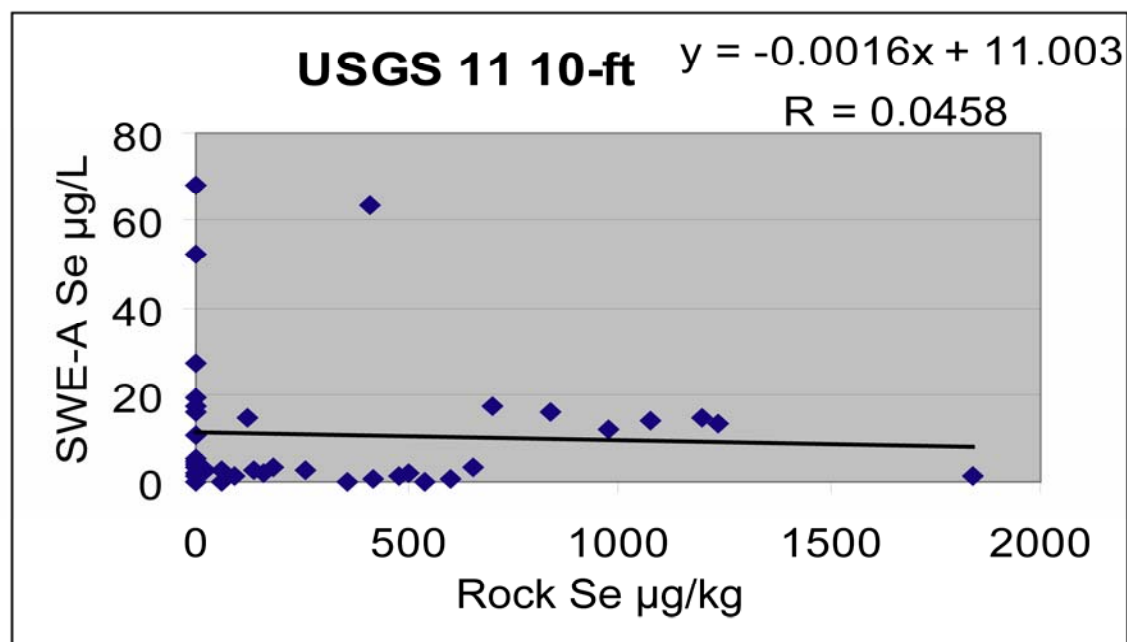
Figure 20. Se concentration (µg/L) in sequential water extraction first extract (SWE-A) versus Se concentration (µg/kg) in rock samples from USGS 11-10-ft.

Data are from Appendices B3 and B13.
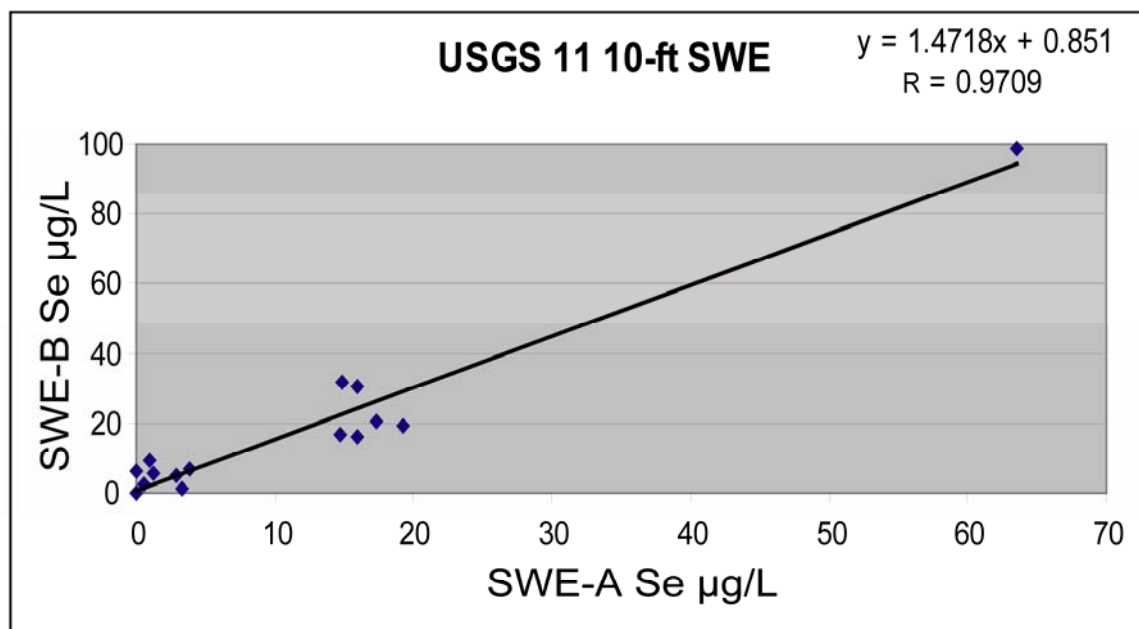
Figure 21. Se concentration (µg/L) in sequential water extraction first extract of rock sub-sample A (SWE-A) versus Se concentration (µg/L) in sequential water extraction first extract of rock sub-sample B (SWE-B) for USGS 11-10-ft samples.

Data are from Appendix B13.
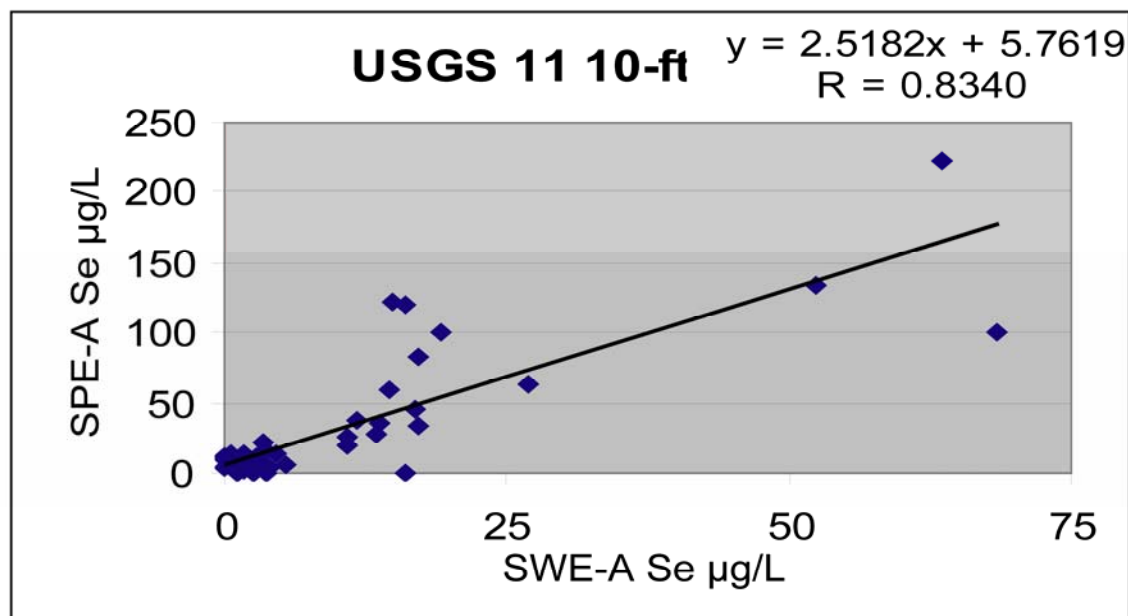
Figure 22. Se concentration (µg/L) in saturated paste extract (SPE-A) versus Se concentration (µg/L) in sequential water extraction first extract (SWE-A) for duplicate sub-samples of rock from USGS 11-10-ft.

Data are from Appendices B11 and B13.
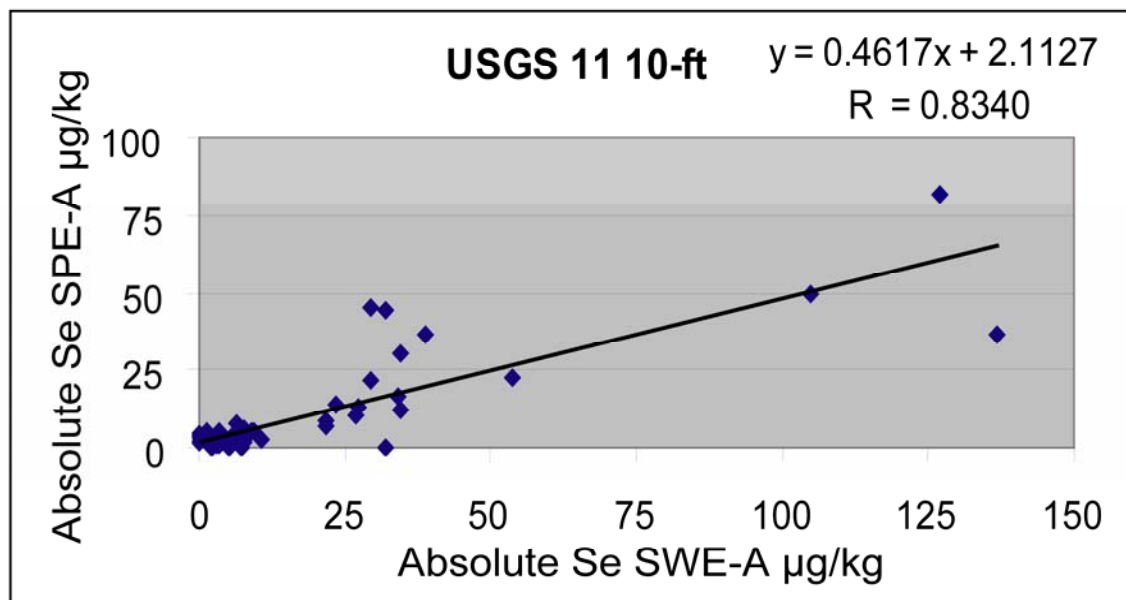
Figure 23. Absolute Se (μg Se in solution / kg of rock leached) in saturated paste extract (SPE-A) versus absolute Se (μg Se in solution / kg of rock leached) in sequential water extraction first extract (SWE-A) for duplicate sub-samples of rock from USGS 11-10-ft.

Data are calculated from Appendices B11 and B13.
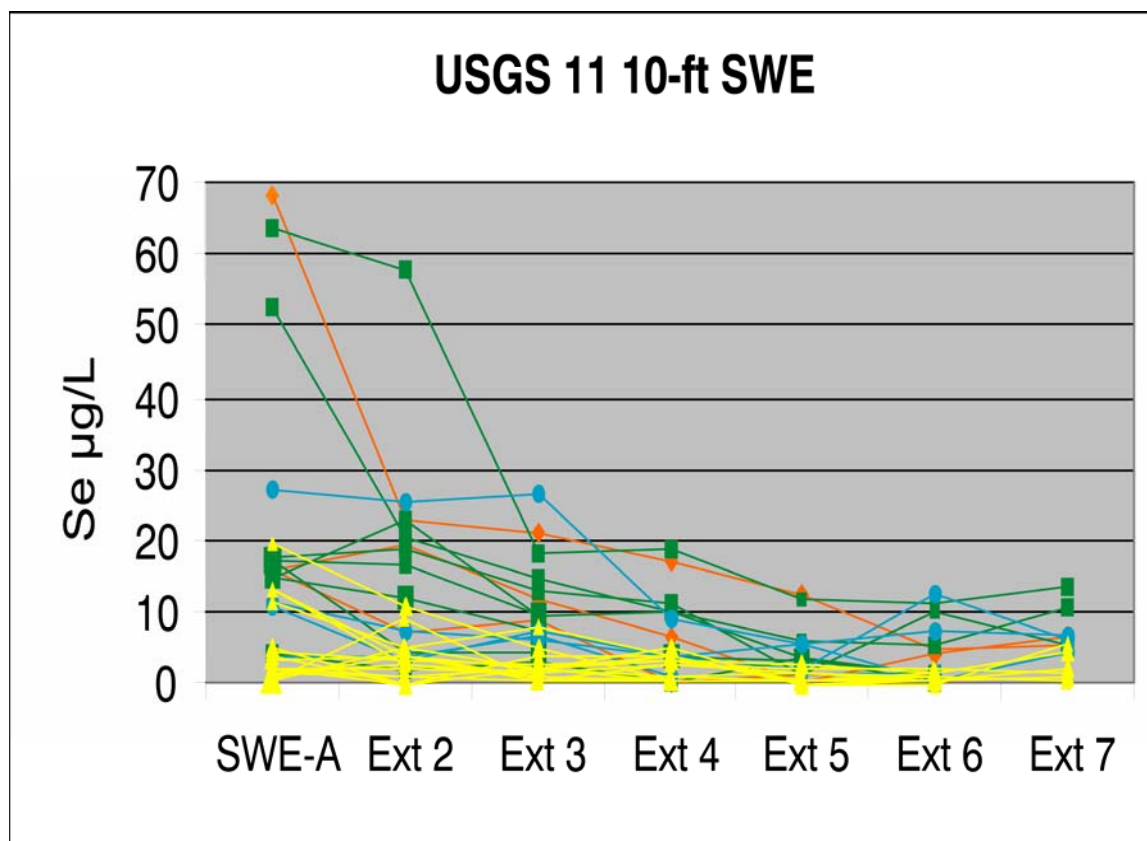
Figure 24. Se concentration (µg/L) in sequential water extractions (SWE-) for up to 7 sequential extractions of a rock sample, for samples from USGS 11-10-ft.

SWE-A is the first extract followed by 2nd, 3rd, 4th, 5th, 6th, and 7th extracts of the same rock material.

Data are from Appendix B13. [claystone = orange, shale = green, siltstone = blue, and sandstone = yellow]

Table 1. Trace element concentrations for 13 elements, including Se, reported in ASTM 3052 with certification by National Institute of Standards and Technology (NIST) for standard reference material (SRM) 2704

ASTM and NIST report the mean concentration and the 95 percent confidence interval (CI 95%) for each element. A normalized metric that is used in this study to indicate precision of results, is the CI 95% divided by the mean concentration. Data are from ASTM 3052 (1996), also available on the web at *http://www.epa.gov/sw-846/pdfs/3052.pdf*.

[values in parens ( ) are not certified; --- = not analyzed or not reported]

Element	Count	ASTM Analyzed		NIST Analyzed		ASTM	NIST
		Mean µg/g	CI 95%	Mean µg/g	CI 95%	CI÷Mean	CI÷Mean
As	4	23.4	2.6	23.4	0.8	0.11	0.03
Cd	6	3.5	1.2	3.45	0.22	0.34	0.06
Cr	6	132.9	1.3	135	5	0.01	0.04
Cu	6	98.0	4.2	98.6	5.0	0.04	0.05
Pb	6	155	9.2	161	17	0.06	0.11
Hg	4	1.49	0.14	1.44	0.07	0.09	0.05
Ni	6	43.6	3.9	44.1	3.0	0.09	0.07
P	4	1016	16	998	28	0.02	0.03
Se	**4**	**1.13**	**0.9**	**(1.1)**	**---**	**0.80**	**---**
S	4	3.56	0.16	---	---	0.04	---
Tl	4	1.15	0.22	1.2	0.2	0.19	0.17
U	4	2.97	0.04	3.13	0.13	0.01	0.04
Zn	6	441.9	0.8	438	12	0.002	0.03

Table 2. Comparison of Se concentration in 12 samples coincident to both USGS 9-LITH and USGS 9-10-ft

The table indicates that the Se concentrations for samples selected by lithology (USGS 9-LITH) tend to be lower than the Se concentrations for samples collected at 10-foot intervals (USGS 9-10-ft). The correlation coefficient (R = 0.6712) is significant at the 0.05 level. However, the correlation is not significant at the 0.01 level. In order to test the equality of the means (mean Se concentration in USGS 9-LITH and mean Se concentration in USGS 9-10-ft), the variances must first be evaluated for equality with an F-test. Depending on the outcome of the F-test, either the variances are equal (E) or they are unequal (UE). Then a t-test tests for equality of the means (using the appropriate t-value for either equal or unequal variances) to determine if the means are equal (E) or unequal (UE). The variance of Se concentrations in USGS 9-LITH samples is equal to the variance of Se concentrations in USGS 9-10-ft samples. The mean Se concentration of USGS 9-LITH samples is equal to the mean Se concentration of USGS 9-10-ft samples.

[data are from Appendices B1 and B2; StdDev = standard deviation; ND = not detected and a value of 0 was used in calculations]

Sample ID interval ft	USGS 9 -LITH Se µg/kg	USGS 9 -10-ft Se µg/kg	USGS 9 -LITH vs 9-10-ft	Lithology	
163-163	540	740	Lower	Siltstone
170-171	100	700	Lower	Siltstone
280-281	1140	1440	Lower	Siltstone
340-341	640	580	Higher	Sandstone
390-391	480	20	Higher	Sandstone
430-431	ND	400	Lower	Sandstone
460-461	ND	ND	ND	Mudstone
560-561	380	1520	Lower	Shale
570-571	120	ND	Higher	Shale
580-581	ND	ND	ND	Sandstone
600-601	ND	140	Lower	Claystone
650-651	ND	180	Lower	Sandstone

USGS 9

$y = 1.0085x + 190.91$

$R^2 = 0.4505$
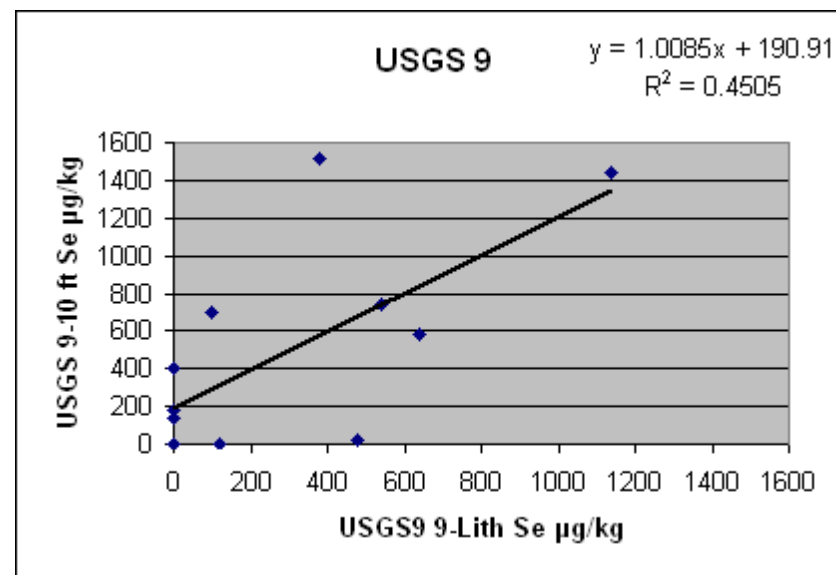
Table 2. cont.

	USGS 9 -LITH	USGS 9 -10-ft
	Se µg/kg	Se µg/kg
Mean	283	477
StdDev	361	543
Median	110	290
Minimum	0	0
Maximum	1140	1520
Count	12	12
CI 95%	204	307

Compare	USGS 9-LITH vs USGS 9 10-ft
	Variance / Mean
	E / E

Critical Values: F 0.05 (11, 11) = 3.47 and T 0.05 (22) = 2.074
Calculated Values: F = 2.262 and T = 1.031
Calculated values are < critical values
Therefore variances are equal (E) to one another, as are the means

Table 3. Se concentrations in duplicate samples and replicate analyses of 12 samples coincident to both USGS 9-LITH and USGS 9-10-ft

Three replicate analyses (designated 1, 2, and 3) were conducted on each of 3 sub-samples (designated A, B, and C) of 12 samples. The 95 percent confidence interval (CI 95%) is an estimate of the precision of the mean Se concentration for the analytical method. The CI 95% divided by the mean is a normalized metric that can be used to compare relative dispersion of the mean, which can be used to compare the precision of Se concentration measurements for samples with differing Se concentrations.

[calculations use data in Appendix B14; StdDev = standard deviation; count = number of analyses; CI 95% = 95 percent confidence interval; CI 95% ÷ Mean = normalized metric used in this study]

Sample ID Interval ft	Mean Se µg/kg	StdDev	Count	CI 95%		CI÷Mean
163-164	453	461	9	301		0.66
170-171	524	613	9	400		0.76
280-281	631	515	9	337		0.53
340-341	149	270	9	176		1.18
390-391	196	344	9	225		1.15
430-431	433	628	9	410		0.95
460-461	269	335	9	219		0.81
560-561	600	657	9	429		0.72
570-571	373	437	9	286		0.77
580-581	329	325	9	212		0.65
600-601	267	280	9	183		0.69
650-651	273	288	9	188		0.69
					Mean =	**0.80**

Table 4. A test for stratigraphic variation of Se concentration, comparing the upper stratigraphic interval to the lower stratigraphic interval in each core (USGS 9-LITH, USGS 9-10-ft, USGS 11-10-ft, and USGS 12-10-ft), using univariate statistics and t-test comparisons

In order to compare the equality of the mean Se concentration in two stratigraphic intervals in each core, the variances must first be evaluated for equality with an F-test. Depending on the outcome of the F-test, either the variances are equal (E) or they are unequal (UE). Then a t-test is used to test for equality of the means (using the appropriate t-value for either equal or unequal variances) and determines if the mean Se concentrations in upper and lower stratigraphic intervals are equal (E) or unequal (UE).

For USGS 9-LITH, the mean Se concentration in the upper interval is greater than in the lower interval (variances are unequal to one another and the means are unequal).

For USGS 9-10-ft, the mean Se concentration in the upper interval is greater than in the lower interval (variances are equal to one another whereas the means are unequal).

For USGS 11-10-ft, the mean Se concentration in the upper interval is equal to the mean Se concentration in the lower interval (variances are equal to one another and the means are equal).

For USGS 12-10-ft, the mean Se concentration in the upper interval is equal to the mean Se concentration in the lower interval (variances are equal to one another and the means are equal).

[calculated from data in Appendices B1, B2, B3, and B4 (with Se values below detection limit set = 0); USGS 9-10-ft includes 1-ft samples selected close to coal beds; USGS 9-10-ft lower stratigraphic interval does not include high Se value 6820 μg/kg; StdDev = standard deviation; CI 95% = 95 percent confidence interval]

Upper Stratigraphic Interval (below Stockton A to above Chilton A)

Core Interval	USGS 9-LITH 114-446 ft Se μg/kg	USGS 9-10-ft 114-446 ft Se μg/kg	USGS 11-10-ft 239-652 ft Se μg/kg	USGS 12-10-ft 316-492 ft Se μg/kg
Mean	553	666	259	346
StdDev	456	425	327	335
Median	480	610	119	320
Minimum	0	0	0	0
Maximum	2440	1820	1200	1060
Count	46	38	41	17
CI 95%	132	135	100	159

Lower Stratigraphic Interval (below Chilton A to above Fire Clay)

Core Interval	USGS 9-LITH 448-690 ft Se μg/kg	USGS 9-10-ft 448-690 ft Se μg/kg	USGS 11-10-ft 653-828 ft Se μg/kg	USGS 12-10-ft 493-625 ft Se μg/kg
Mean	64	329	114	167
StdDev	163	518	203	264
Median	0	0	0	10
Minimum	0	0	0	0
Maximum	820	1620	540	740
Count	53	22	18	12
CI 95%	44	216	94	149

Table 4. cont.

Compare Upper Stratigraphic Interval versus Lower Stratigraphic Interval			
USGS 9-LITH **Upper vs Lower** **Variance / Mean**	**USGS 9-10-ft** **Upper vs Lower** **Variance / Mean**	**USGS 11-10-ft** **Upper vs Lower** **Variance / Mean**	**USGS 12-10-ft** **Upper vs Lower** **Variance / Mean**
UE / UE	E / UE	E / E	E / E

Table 5. A test for regional variation of Se concentration in each stratigraphic interval (upper and lower) compared among cores, using univariate statistics and t-test comparisons

In order to compare the equality of the mean Se concentration in each stratigraphic interval, the variances must first be evaluated for equality with an F-test. Depending on the outcome of the F-test, either the variances are equal (E) or they are unequal (UE). Then a t-test tests for equality of the means (using the appropriate t-value for either equal or unequal variances) and determines if the mean Se concentrations are equal (E) or unequal (UE).

For the upper stratigraphic interval: 1) the mean Se concentration in USGS 9-LITH is equal to the mean Se concentration in USGS 9-10-ft and USGS 12-10-ft (for both comparisons variances are equal to one another and means are equal), and greater than in USGS 11-10-ft (variances are unequal and the means are unequal) 2) the mean Se concentration in USGS 9-10-ft is greater than in USGS 11-10-ft and USGS 12-10-ft (for both comparisons variances are equal to one another and the means are unequal); and 3) the mean Se concentration in USGS 11-10-ft is equal to USGS 12-10-ft (variances are equal to one another and the means are equal).

For the lower stratigraphic interval: 1) the mean Se concentration in USGS 9-LITH is greater than the mean Se concentration in USGS 9-10-ft (the variances are unequal, as well as the means), and is equal to the mean Se concentration in USGS 11-10-ft (variances are equal to one another and means are equal) and USGS 12-10-ft (variances are unequal and the means are equal); 2) the mean Se concentration in USGS 9-10-ft is equal to USGS 11-10-ft and USGS 12-10-ft (for both comparisons variances are unequal to one another and the means are equal); and 3) the mean Se concentration in USGS 11-10-ft is equal to USGS 12-10-ft (variances are equal to one another and the means are equal).

[calculated from data in Appendices B1, B2, B3, and B4 (with Se values below detection limit set = 0); USGS 9-10-ft includes 1-ft samples selected close to coal beds; USGS 9-10-ft lower stratigraphic interval does not include high Se value 6820 μg/kg; StdDev = standard deviation; CI 95% = 95 percent confidence interval]

Upper Stratigraphic Interval (below Stockton A to above Chilton A) univariate statistics

	Core Interval	USGS 9-LITH 114-446 ft Se μg/kg	USGS 9-10-ft 114-446 ft Se μg/kg	USGS 11-10-ft 239-652 ft Se μg/kg	USGS 12-10-ft 316-492 ft Se μg/kg
Mean		553	666	259	346
StdDev		456	425	327	335
Median		480	610	119	320
Minimum		0	0	0	0
Maximum		2440	1820	1200	1060
Count		46	38	41	17
CI 95%					
Table 5 cont.		132	135	100	159

Compare Upper Stratigraphic Intervals, F-test / t-test (variance / mean)

	USGS 9-LITH	USGS 9-10-ft	USGS 11-10-ft	USGS 12-10-ft
USGS 9-LITH	--	E / E	UE / UE	E / E
USGS 9-10-ft	--	--	E / UE	E / UE
USGS 11-10-ft	--	--	--	E / E

Lower Stratigraphic Interval (below Chilton A to above Fire Clay) univariate statistics

	Core Interval	USGS 9-LITH 448-690 ft Se µg/kg	USGS 9-10-ft 448-690 ft Se µg/kg	USGS 11-10-ft 653-828 ft Se µg/kg	USGS 12-10-ft 493-625 ft Se µg/kg
Mean		64	329	114	167
StdDev		163	518	203	264
Median		0	0	0	10
Minimum		0	0	0	0
Maximum		820	1620	540	740
Count		53	22	18	12
CI 95%		44	216	94	149

Compare Lower Stratigraphic Intervals, F-test / t-test (variance / mean)

	USGS 9-LITH	USGS 9-10-ft	USGS 11-10-ft	USGS 12-10-ft
USGS 9-LITH	--	UE / UE	E / E	UE / E
USGS 9-10-ft	--	--	UE / E	UE / E
USGS 11-10-ft	--	--	--	E / E

Table 6. Frequency distribution and univariate statistics for Se concentration data in all samples collected at 10-foot intervals in USGS 9-10-ft, USGS 11-10-ft, and USGS 12-10-ft

A. Univariate statistics are calculated for all Se concentrations.

B. Univariate statistics are calculated for Se concentrations without the two highest Se values.

C. Univariate statistics are calculated for Se concentrations without the two highest Se values and replacing 0 values (not detected) with 5 (half the detection limit).

[calculated from data in Appendices B2, B3, and B4 (with Se values below detection limit set = 0 unless otherwise noted); USGS 9-10-ft includes 1-ft and p-ft samples (see Appendix B2); StdDev = standard deviation; CI 95% = 95 percent confidence interval]

Se µg/kg	Frequency	Percent	Cumulative Percent
0	78	33.1	33.1
10	2	0.8	33.9
20	5	2.1	36.0
54	1	0.4	36.4
60	4	1.7	38.1
80	2	0.8	39.0
90	1	0.4	39.4
100	6	2.5	41.9
115	1	0.4	42.4
119	1	0.4	42.8
120	2	0.8	43.6
124	1	0.4	44.1
140	3	1.3	45.3
160	3	1.3	46.6
180	5	2.1	48.7
193	1	0.4	49.2
200	3	1.3	50.4
220	3	1.3	51.7
233	1	0.4	52.1
240	1	0.4	52.5
260	1	0.4	53.0
272	1	0.4	53.4
280	1	0.4	53.8
285	1	0.4	54.2
300	3	1.3	55.5
320	5	2.1	57.6
340	2	0.8	58.5
355	1	0.4	58.9
360	3	1.3	60.2
371	1	0.4	60.6
380	1	0.4	61.0
400	6	2.5	63.6
413	1	0.4	64.0
420	1	0.4	64.4
440	2	0.8	65.3
460	2	0.8	66.1
480	3	1.3	67.4
500	2	0.8	68.2

A. All Data

	Se µg/kg
Mean	406
StdDev	628
Median	200
Minimum	0
Maximum	6820
Count	236
CI 95%	80

B. Remove 2 high Se values (6820 and 3300)

	Se µg/kg
Mean	366
StdDev	428
Median	200
Minimum	0
Maximum	1840
Count	234
CI 95%	55

C. Remove 2 high Se values (6820 and 3300) and change 0 values to 5

	Se µg/kg
Mean	368
StdDev	427
Median	200
Minimum	5
Maximum	1840
Count	234
CI 95%	55

520	2	0.8	69.1
540	2	0.8	69.9
560	4	1.7	71.6
580	3	1.3	72.9
600	5	2.1	75.0
620	1	0.4	75.4
640	1	0.4	75.8
660	4	1.7	77.5
680	1	0.4	78.0
700	3	1.3	79.2
708	1	0.4	79.7
720	1	0.4	80.1
739	1	0.4	80.5
740	3	1.3	81.8
760	1	0.4	82.2
777	1	0.4	82.6
780	1	0.4	83.1
800	3	1.3	84.3
820	1	0.4	84.7
840	2	0.8	85.6
860	1	0.4	86.0
900	2	0.8	86.9
940	2	0.8	87.7
960	2	0.8	88.6
980	1	0.4	89.0
1000	1	0.4	89.4
1040	3	1.3	90.7
1060	1	0.4	91.1
1080	1	0.4	91.5
1100	1	0.4	91.9
1140	2	0.8	92.8
1200	2	0.8	93.6
1240	2	0.8	94.5
1260	1	0.4	94.9
1320	1	0.4	95.3
1380	1	0.4	95.8
1440	1	0.4	96.2
1500	1	0.4	96.6
1520	2	0.8	97.5
1540	1	0.4	97.9
1620	1	0.4	98.3
1820	1	0.4	98.7
1840	1	0.4	99.2
3300	1	0.4	99.6
6820	1	0.4	100.0
Total	**236**	**100.0**	

Table 7. A test for lithologic variation of Se concentration in four dominant lithologies in USGS 9-LITH and USGS 9-10-ft samples, using univariate statistics and t-test comparison

The four dominant lithologies are claystone (CLST), shale (SH), siltstone (SLST), sandstone (SS).

Rank order of means in USGS 9-LITH is SLST > SS > SH > CLST. T-test comparison of mean Se concentrations among lithologies in USGS 9-LITH is as follows: CLST = SH, CLST < SLST, CLST < SS, SH < SLST, SH < SS, SLST = SS.

Rank order of means in USGS 9-10-ft is SLST > SS > CLST > SH. T-test comparison of mean Se concentration among lithologies in USGS 9-10-ft is as follows: CLST = SH, CLST < SLST, CLST = SS, SH = SLST, SH = SS, SLST > SS.

[calculated from data in Appendices B1 and B2 (with Se values below detection set = 0); USGS 9-10-ft includes 1-ft samples and does not include high outlier Se = 6820 μg/kg in a sandstone sample; StdDev = standard deviation; CI 95% = 95 percent confidence interval]

USGS 9-LITH, univariate statistics

	Claystone Se μg/kg	Shale Se μg/kg	Siltstone Se μg/kg	Sandstone Se μg/kg
Mean	33	65	523	322
StdDev	100	144	605	333
Median	0	0	400	250
Minimum	0	0	0	0
Maximum	300	540	2440	1000
Count	9	20	23	48
CI 95%	65	63	247	94

USGS 9-LITH, F-test / t-test

	Variance / Mean		
	Shale	Siltstone	Sandstone
Claystone	E / E	UE / UE	UE / UE
Shale	--	UE / UE	UE / UE
Siltstone	--	--	UE / E

Table 7. cont.

USGS 9-10-ft, univariate statistics

	Claystone Se µg/kg	Shale Se µg/kg	Siltstone Se µg/kg	Sandstone Se µg/kg
Mean	464	405	943	467
StdDev	506	745	547	395
Median	200	50	740	400
Minimum	0	0	320	0
Maximum	1320	1520	1820	1620
Count	10	4	7	52
CI 95%	314	730	405	107

USGS 9-10-ft, F-test / t-test

	Variance / Mean		
	Shale	Siltstone	Sandstone
Claystone	E / E	E / UE	E / E
Shale	--	E / E	UE / E
Siltstone	--	--	E / UE

Table 8. A test for lithologic variation of Se concentration in roof, parting, and floor samples from USGS 9, using univariate statistics and t-test comparisons

The means are equal to one another for the 3 sample groups: roof = parting = floor.

[calculated from data in Appendix B9; StdDev = standard deviation; CI 95% = 95 percent confidence interval]

Univariate Statistics

	Roof Se µg/kg	Parting Se µg/kg	Floor Se µg/kg
Mean	798	1280	922
StdDev	732	649	1020
Median	550	1180	600
Minimum	140	500	0
Maximum	1940	2300	3340
Count	8	5	13
CI 95%	507	569	555

F-test / t-test

	Variance / Mean	
	Parting	Floor
Roof	E / E	E / E
Parting	--	E / E

Table 9. Se concentration in USGS 9-RPF (combined roof, parting and floor samples from USGS 9), univariate statistics

[calculated from data in Appendix B9; StdDev = standard deviation; CI 95% = 95 percent confidence interval]

Univariate Statistics	
	RPF **Se µg/kg**
Mean	952
StdDev	864
Median	660
Minimum	0
Maximum	3340
Count	26
CI 95%	332

Table 10. A test for lithologic variation in Se concentration between USGS 9-RPF, roof, parting, and floor samples and four dominant lithologies in USGS 9-LITH and USGS 9-10-ft samples, using univariate statistics and t-test comparisons

RPF = combined roof, parting, and floor samples. The four dominant lithologies are claystone (= CLST), shale (= SH), siltstone (= SLST), and sandstone (= SS).

In USGS 9-PRF and USGS 9-LITH, rank order of the mean Se concentrations is RPF > SLST > SS > SH > CLST. T-test comparison of mean Se concentrations among RPF and dominant lithologies in USGS 9-LITH is as follows: RPF > CLST, RPF > SH, RPF = SLST, RPF > SS.

In USGS 9-PRF and USGS 9-10-ft, rank order of the mean Se concentrations is RPF > SLST > SS (without high Se value = 6820 µg/kg) > CLST > SH. T-test comparison of mean Se concentrations among RPF and dominant lithologies in USGS 9-10-ft is as follows: RPF > CLST, RPF = SH, RPF = SLST, RPF > SS.

[calculated from data in tables 7, 8, and 9]

USGS 9-LITH, F-test / t-test

	Variance / Mean			
	Claystone	**Shale**	**Siltstone**	**Sandstone**
RPF	UE / UE	UE / UE	E / E	UE / UE
roof	UE / UE	UE / UE	E / E	UE / UE
parting	UE / UE	UE / UE	E / UE	UE / UE
floor	UE / UE	UE / UE	UE / E	UE / UE

USGS 9-10-ft, F-test / t-test

	Variance / Mean			
	Claystone	**Shale**	**Siltstone**	**Sandstone**
RPF	UE / UE	E / E	E / E	UE / UE
roof	E / E	E / E	E / E	UE / E
parting	E / UE	E / E	E / E	E / UE
floor	UE / E	E / E	E / E	UE / UE

Table 11. Comparison of Se concentrations (µg/g or ppm) in various lithologies for published data and data reported in this study

	Claystone Se µg/g	Shale Se µg/g	Siltstone Se µg/g	Sandstone Se µg/g
Horn and Adams (1966), modeled global average				
Mean		0.60		0.525
Minimum		0.3		0.05
Maximum		0.9		1.0
Baedecker and others (1998), western US (see notes below)				
Mean		2.9	2.6	1.5
StdDev		5.7	5.9	7.3
Median		0.70	0.70	0.10
Minimum		0.05	0.10	0.05
Maximum		34	23	100
Count		247	23	672
CI 95%		0.72	2.4	0.56
Mullennex (2005), 5 cores at a mine site in southwest West Virginia				
Mean		0.75		0.09
StdDev		1.23		0.11
Count		102		211
CI 95%		0.24		0.01
This Study (data from Appendices B2, B3, B4), 3 cores (USGS 9-10-ft, 11-10-ft, 12 -10-ft) from southwest West Virginia [USGS 9-10-ft includes 1-ft and p-ft samples; does not include two high Se values 6.82 and 3.30 ppm in sandstone]				
Mean	0.46	0.42	0.56	0.32
StdDev	0.49	0.44	0.56	0.40
Median	0.20	0.32	0.41	0.16
Minimum	0.00	0.00	0.00	0.00
Maximum	1.32	1.52	1.82	1.84
Count	15	33	20	166
CI 95%	0.25	0.15	0.25	0.06

Data from Baedecker and others (1998):

        1) 1439 data points, all shale and sandstone data with Se values

        2) Samples are from western US, including Alaska

        3) Use Geolex (http://ngmdb.usgs.gov/Geolex/geolex_home.html) to determine usage and age range for given information on Formations

        4) Assign dominant lithology and lithologic modifier from Appendix A4.

        5) Negative values are 'less than' values.

        6) Assign the value 0.05 ppm to all negative Se values (289). 0.05 ppm is the absolute value of half the median value for all 'less than' values.

Table 11. cont.

Remove 497 samples:

       1) Samples with "no information" for Formation (16)

       2) Samples with Pre Cambrian for age (217)

       3) Samples with ROOF, PART (parting), and SEAT (floor) for lithology associated with coal beds (all 19 samples from Alaska)

       4) Samples with ROCK (no specific lithology information), SURF MAT (surface material), PYR (pyrite), BREC (breccia), CGL (conglomerate), LS (limestone), and CLST (claystone) for lithology (87)

       5) Samples with lithologic modifier of ORE (ore), U (uranium mineralization), MIN (mineralization, usually sulfate), FEST (ironstone - goethite mineralization), and PYR (pyrite) (158)

The resultant data set, used above, is 942 samples:

       857 range in age from Tertiary to Mississippian

       85 sandstone samples (75 are from Utah) have no age data (no Formation given)

Selenium speciation in soils after alkaline extraction

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Abstract

A speciation method for selenium in soils was developed to evaluate the distribution of Se species by using as an example a seleniferous soil from Ireland. First, a water extraction was applied in order to evaluate the Se fraction directly available to plants. Results have shown that only 2% of the total selenium was water soluble and this fraction contained mainly Se(VI). Then, an alkaline extraction was used to solubilize both humic substances and selenium. After optimization of this procedure, a single extraction with a 2 mol l^{-1} sodium hydroxide solution allowed the extraction of 50% of total Se from the soil, a recovery of 90% was obtained with a 10-step extraction procedure. The alkaline extract was acidified to pH 1.5 to divide the acid-soluble fraction (fulvic acids) from the humic acids fraction precipitated at this pH. Seventy percent of total soluble selenium were found in the fulvic acid fraction while 30% were present in the non-acid-soluble fraction. In each fraction, a speciation procedure was then performed in order to identify and determinate inorganic and organic selenium forms. In the acid-soluble fraction, the main Se form was Se(IV) (approx. 44%), non-negligible amounts of organic Se were found (approx. 41%) and Se(VI) represented approx. 15% of this fraction. In the non-acid-soluble fraction, only Se(IV) was determined and it represented approx. 60% of the total Se contained in this fraction.   © 1997 Elsevier Science B.V.

1. Introduction

Depending on its concentration and chemical form, selenium functions as an essential element or potent toxicant to humans, livestock, plants,

waterfowl and certain bacteria (Nève and Therond, 1991). Soil Se, which usually plays an important role in determining the Se level in food grains, vegetable and even drinking water, is the basis of the Se cycle in the geoecosystem (Mayland et al., 1989; Nève and Therond, 1991; Oldfield, 1992).

Total selenium concentrations in soil range

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from 0.1 μg Se g^{-1} (parts of China and Finland) to 100 μg Se g^{-1} (Ireland and some states of the U.S.) (Mayland et al., 1989; McNeal and Balistrieri, 1989; Nève and Therond, 1991). The concentration depends on the Se content of the parent material, which often increases with depth (Mayland et al., 1989; McNeal and Balistrieri, 1989), closeness to the sea, presence of fine particles and organic matter in the soil (Mayland et al., 1989; McNeal and Balistrieri, 1989; Tam et al., 1995). However, knowledge of the total selenium concentration is not sufficient to evaluate Se availability and toxicity. In soils, selenium generally seems to be present in inorganic forms, in the following oxidation states: selenides [Se($-$II)], elemental Se [Se(0)], selenites [Se(IV)] and selenates [Se(VI)]. It is also possible to find organic selenium compounds. Availabilities of these physico–chemical forms are different and their distribution depends on soil properties such as acidity, aeration, the mineral and organic-matter contents, and the microbiological activity (Elrashidi et al., 1989; Masscheleyn et al., 1990; Oremland et al., 1990; Masscheleyn and Patrick, 1993; Tam et al., 1995; Jayaweera and Biggar, 1996; Zawislanski and Zavarin, 1996).

As soil is a complex multi-element system affected by many unstable factors, there is no commonly accepted research method suitable for studying Se speciation. Furthermore, the extraction reagent used must not modify the distribution of the physico–chemical forms of this element. Agronomists have for a long time used treatments intended to evaluate selenium fractions playing a particular role towards Se availability to plants. Hot water extraction is applicable to non-adsorbed selenium and selenium related to water-soluble organic matter (Wang and Sippola, 1990; Yamada and Hattori, 1990). Other treatments with the acid ammonium acetate — EDTA mixture (Wang and Sippola, 1990), Na$_2$SO$_4$ (Yamada and Hattori, 1990) or KH$_2$PO$_4$ (Gustafsson and Johnsson, 1992; Chao and Sanzolone, 1989) also release the exchangeable Se. These extraction procedures make possible the solubilization of 0.5–7% of total Se according to the studied soil (Yamada and Hattori, 1989, 1990; Gustafsson and Johnsson, 1992).

The acid extraction procedures [2 mol l^{-1} HNO$_3$ (Kang et al., 1991) or 4 mol l^{-1} HCl (Chao and Sanzolone, 1989)] removes selenium associated with calcium compounds or minerals and acid-soluble organic matter. The total Se solubilized ranges from 5 to 30% in function of the studied soil.

The alkaline extractions with sodium hydroxide permit the solubilization of selenium bound to humic substances (Cutter, 1985; Kang et al., 1991), clays (Bar-Yosef and Meek, 1987) and/or manganese, iron and aluminium oxyhydroxide (Barrow, 1992; Tam et al., 1995). Selenium extraction recoveries are higher, from 30% (Kang et al., 1991; Abrams and Burau, 1989) to 95% (Kang et al., 1991, 1993) depending on the soils characteristics.

It is also possible to evaluate the Se soil availability by using sequential fractionation (Chao and Sanzolone, 1989; Gustafsson and Johnsson, 1992; Tan et al., 1994; Manning and Burau, 1995; Zhang and Moore, 1996). The first steps are the ones described previously (non-adsorbed Se, exchangeable Se, Se associated with calcium compounds and Se bound to organic matter). Other fractions concerning Se bound to sulfides (KClO$_3$-HCl) (Chao and Sanzolone, 1989), Se associated with iron compounds (sodium citrate) (Tan et al., 1994), Se located in the internal parts of Fe and Al oxides or minerals (sodium dithionite) (Tan et al., 1994), Se associated with reducible oxide (NH$_2$OH.HCl) (Manning and Burau, 1995) or elemental Se (Na$_2$SO$_3$ 1 mol l^{-1}) (Zhang and Moore, 1996) can also be extracted from the soil. In each case, the last step is an acid digestion to obtain the total residual Se (Chao and Sanzolone, 1989; Tan et al., 1994; Manning and Burau, 1995; Zhang and Moore, 1996).

Some authors consider that the non-adsorbed Se, the exchangeable Se and the Se associated to organic matter steps correspond to non-enveloped Se, which is available to plants (Yamada and Hattori, 1990; Gustafsson and Johnsson, 1992; Kang et al., 1991; Tan et al., 1994). For these reasons, a solubilization method of selenium by alkaline extraction is described in this study and a speciation procedure is developed in the extracts in order to identify and determinate a maximum

of inorganic and organic selenium forms in a seleniferous soil from Ireland.

2. Experimental

2.1. Analytical methods used for Se determination

In this work, two analytical methods were used to determine only Se in the + IV oxidation state. The first method, Differential Pulse Cathodic Stripping Voltammetry (DPCSV) is an electrochemical method based on the deposition of a mercury (II) selenide film on a hanging mercury drop electrode.

The principle of the hydride generation — quartz furnace atomic absorption spectrometry (HG-QFAAS) method is as follows. The reducing agent ($NaBH_4$) is added in the generator vessel to form selenium hydride (SeH_2) in acid medium from Se(IV). Then, SeH_2 is flushed by the carrier gas (He) and after a cryogenic trapping, is detected by atomic absorption spectrometry equipped with a quartz furnace in a H_2/O_2 flame.

These two analytical methods have been previously described and optimized in our laboratory (Lespes et al., 1994; Potin Gautier et al., 1994; Séby and Potin Gautier, 1996). The retained operating conditions in this work for the DPCSV and HG-QFAAS methods are listed in Table 1.

These methods have been applied to a white clover sample certified for its total Se content (CRM 402) (Quevauviller et al., 1992). Taking into account standard deviations, the Se concentrations obtained by DPCSV (6.87 ± 0.41 μg Se g^{-1}) (Séby and Potin Gautier, 1996) and HG-QFAAS (6.9 ± 0.6 μg Se g^{-1}) (Lespes et al., 1994) are in good agreement with the BCR certified value (6.70 ± 0.45 μg Se g^{-1}).

All analyses have been performed in triplicate, and from triplicate analyses standard deviation have been calculated

2.2. Instrumentation

The DPCSV analyses were performed on a PAR apparatus comprising a voltammetric analyzer (Model 264A) in connection with the PAR Model 303 A device (hanging mercury drop electrode, silver/silver chloride/saturated KCl, saturated in AgCl reference electrode and platinum auxiliary electrode) and a magnetic stirrer PAR 305. Data were displayed on a Kipp and Zonen recorder.

The HG-QFAAS apparatus included a hydride generator vessel with a magnetic stirrer, an empty glass column (4-mm i.d.) with a square form (705-mm total length, 35-mm base width) used as a SeH_2 cryogenic trap. Detection is performed with

Table 1

Operating conditions for Se(IV) determination by DPCSV and HG-QFAAS

DPCSV		HG-QFAAS	
Supporting electrolyte	H_2SO_4 0.1 mol l^{-1}	Analytical medium	HCl 4 mol l^{-1}
Volume of solution		Volume of solution	
in the analysis cell	10 ml	in the reactor	50 ml
Purge time	8 min	Reactor temperature	20°C
Initial potential	$E_i = -0.2$ V	$NaBH_4$ flow-rate	2 ml min^{-1}
Final potential	$E_f = -0.7$ V	$NaBH_4$ flow-time	180 s
Pulse amplitude	$\Delta E = 50$ mV	Furnace temperature	800°C
Scan rate	v = 5 mV s^{-1}	Helium flow-rate	400 ml min^{-1}
Deposition time	120 s	Oxygen flow-rate	40 ml min^{-1}
Rest time	30 s	Hydrogen flow-rate	300 ml min^{-1}
Potential of the film		Absorption wavelength	196.0 nm
deposition peak		Retention time of the SeH_2 peak	30s
	$E_{peak} = -0.45$ V	Se(IV) detection limit	
Se(IV) detection limit		in pure medium	30 ng l^{-1}
in pure medium	25 ng l^{-1}		

a quartz tube atomizer (140-mm length, 12-mm i.d.) placed in a furnace (Perkin Elmer MHS 1) and a Varian SpectrAA-10 atomic absorption spectrometer. Data are recorded with a Shimadzu CR4A-Chromatopac integrator equipped with a PC16N I/O card for the automatization of the whole process.

2.3. Reagents

The Se(IV), Se(VI), selenomethionine and selenocystine stock solutions (1000 mg l^{-1}) were prepared monthly from sodium selenite (Na$_2$SeO$_3$.5H$_2$O; Merck suprapure), sodium selenate (Na$_2$SeO$_4$ 98%; Aldrich suprapure), seleno-DL-methionine and seleno-DL-cystine (Sigma), respectively. All these solutions were stored in Teflon bottles at + 4°C. Working solutions (10 mg l^{-1} and 100 μg l^{-1}) were prepared daily.

The analytical media used for DPCSV (H$_2$SO$_4$ 96%) and HG-QFAAS (HCl 37%) were prepared with Merck suprapure reagents.

For the HG-QFAAS determinations, the reducing solution was prepared with sodium tetrahydroborate (NaBH$_4$; Fluka) (10% m/v) and stabilized by the addition of 1% (m/v) NaOH (Merck suprapure). The solution was stored at + 4°C after decantation.

The different reagents used for the digestions (HNO$_3$ 65%, H$_2$O$_2$ 30%), the reduction of Se(VI) (HCl 37%) and for soil extraction (NaOH) were Merck suprapure products.

All solutions were prepared with suprapure water (18 MΩ) obtained from a Millipore system (MilliRO followed by MilliQ).

2.4. Determination of the Se forms in solution

The concentrations of different Se species have been determined according to the procedure illustrated in Fig. 1.

Direct analysis by DPCSV or HG-QFAAS allows the determination of the Se(IV) concentration. Se(VI) concentration is determined after reduction into the Se(IV) form. The optimal reduction yield was obtained with 6 mol l^{-1} HCl at 90°C in sealed glass tubes using a hot water bath
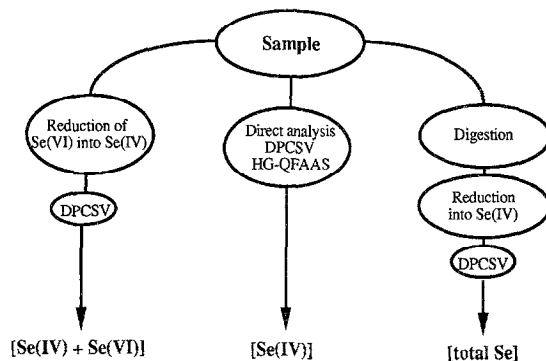
Fig. 1. Speciation schema of selenium in solution.

for 45 min. The Se(VI) concentration is then obtained from the difference between the mean values of the sum [Se(IV) + Se(VI)] and [Se(IV)].

The total selenium content is determined after a digestion of samples with a HNO$_3$/H$_2$O$_2$ mixture (2:1, v/v, respectively). This mixture is evaporated to dryness on a hot plate and the residue is then dissolved in 10 ml of suprapure water. Selenium contained in the digested extract is reduced into the Se(IV) form and analyzed.

2.5. Soil sample

The studied soil comes from a seleniferous area in Ireland. It is a neutral soil (pH 7.25) with a 4.70% organic carbon content. Its total selenium concentration has been determined by an interlaboratory program organized in 1991 by the MRT (French Research and Technology Office) (Potin-Gautier et al., 1991). A total Se concentration of (5.92 ± 0.50) μg Se g^{-1} has been determined.

2.6. Soil Se extraction procedure

The alkaline extraction was carried out as follows: 10 ml of sodium hydroxide solution (the NaOH concentration applied is optimized later on) are added to 1 g of soil in a closed flask. This mixture is submitted to stirring by sonication and centrifuged (4000 rpm) for 20 min.

The Se(IV) and total Se concentrations are determined in the supernatant according to Fig. 1 and the soil residue is analyzed for its total Se

Table 2
Selenium distribution in the soil-water extract

[Total Se] (μg Se g^{-1}) $\pm \sigma_n$ ($n = 3$)	[Se(IV)] (μg Se g^{-1}) $\pm \sigma_n$ ($n = 3$)	[Se(VI)] (μg Se g^{-1}) $\pm \sigma_n$ ($n = 3$)
0.117 ± 0.007	0.0327 ± 0.0007	0.078 ± 0.007

content. The extraction by water was carried out in the same way by replacing the hydroxide sodium solution by suprapure water.

2.7. Fractionation of the alkaline extract

The pH of the supernatant was adjusted to 1.5 with 1 mol l^{-1} sulphuric acid. After standing for 30 min, the acid-soluble fraction (FA) was separated from the precipitated fraction (HA) by centrifugation (20 min, 4000 rpm).

In the acid-soluble fraction, determination of the different Se forms is determined according to the procedure presented in Fig. 1. The non-acid-soluble fraction is analyzed for its total Se content and the Se(IV) concentration is determined by HG-QFAAS after dissolution of the precipitate in 10 ml of a 2 mol l^{-1} NaOH solution.

3. Results and discussion

3.1. Soil water-soluble selenium

An extraction with water was first applied to the soil. The total Se recovery and the Se speciation results are given in Table 2.

The Se total extraction recovery is (2.0 ± 0.1%). This proportion is low, but its determination is interesting because water-soluble soil Se is one of the major Se fraction that can be used by organisms. It also affects human and animal health by governing the Se content in drinking water and grains (Yamada and Hattori, 1989; Wang and Sippola, 1990; Yamada and Hattori, 1990; Tan et al., 1994).

Considering the speciation results and taking into account the standard deviations, this fraction mainly consists of selenites and selenates ([Se(IV) + Se(VI)] = 95 ± 6%). Selenates are the major species (67 ± 6%) with regard to selenites (28.0 ± 0.6%). As it is shown in literature, Se(VI) is less

fixed in soil than Se(IV) consequently its solubilization in water and its availability are easier (Bar-Yosef and Meek, 1987; Läuchly, 1993; Masscheleyn and Patrick, 1993).

3.2. Selenium speciation after alkaline extraction

3.2.1. Alkaline extraction of soil Se

Literature shows that the alkaline extraction can be used to obtain both the best Se recoveries and a good evaluation of the availability of Se from the soil (Abrams and Burau, 1989; Kang et al., 1991, 1993), this procedure has therefore been considered.

To obtain a maximal and reproducible Se extraction from the soil, different parameters have been studied, such as NaOH concentration (from 0.5 to 4 mol l^{-1}), the sonication stirring time (from 15 to 270 min) and the kind of flask material (glass or Teflon) submitted to stirring by sonication.

The maximal Se extraction recovery has been obtained by adding 10 ml of a 2 mol l^{-1} NaOH solution in a closed Teflon flask. The use of sodium hydroxide solutions at concentrations greater than 2 mol l^{-1} does not extract greater quantities of selenium from the soil, but induced a more important solubilization of organic matter making digestions less easy to perform.

The flask was maintained in the sonication bath for a period of 3 h. The Se extraction of the soil sample for longer periods of time does not result in an appreciable increase in the concentration of total Se found in the leachate.

With these conditions, the total selenium concentration extracted is 2.94 ± 0.07 μg Se g^{-1} with a repeatability (expressed as % R.S.D.) of 2.5% from six independent extractions (the recovery is 50 ± 1%). The total Se content in the solid residue is 3.0 ± 0.2 μg Se g^{-1}. Hence, the total Se recovery in the soil is quantitative 100 ± 4% indicating
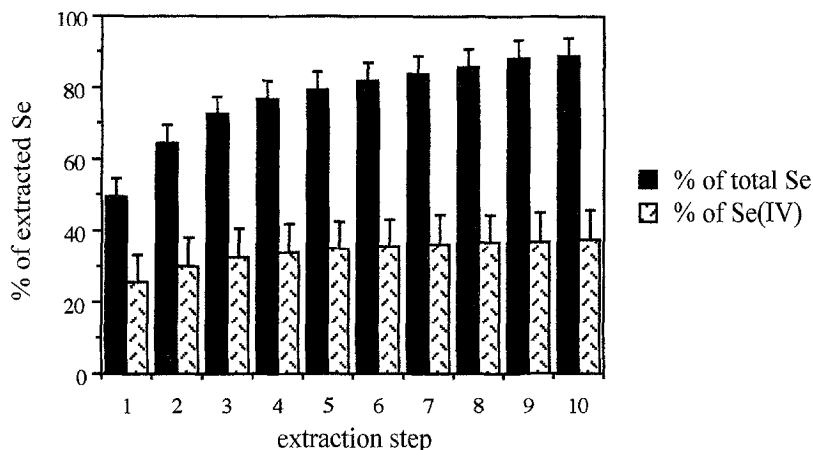
Fig. 2. Repeated extractions of soil with a 2 mol l^{-1} NaOH solution.

that no losses occurred during this single-step extraction procedure.

In order to improve Se solubilization, a procedure using repeated extractions from the same soil sample has been applied. The operating conditions used are those described before.

Results obtained from 10 consecutive extractions are presented in Fig. 2. The major part of the total Se is recovered by a single extraction with a 2 mol l^{-1} sodium hydroxide solution and the amount of extracted Se decreases with the repetition of the extraction. The total Se recovered by the 10-step extraction procedures is 90% of the total Se content of the soil.

The Se fraction that has not been extracted after this treatment (approx. 10% of total soil Se) is assumed to be linked to humins or soil inorganic particles (Kang et al., 1993; Masscheleyn and Patrick, 1993).

Given the highly alkaline conditions and elevated temperature of the extraction procedure, the more important release of selenium from the soil with the repetition of extraction could be the result of a slow and progressive oxidation of Se(−II) or Se(0) to selenite or selenate, more soluble. Furthermore, a soil is a complex medium and the presence of influent factors can promote these oxidation reactions.

The Se(IV) concentration in each of the successive extracts has also been determined by HG-QFAAS. Results (Fig. 2) show that the Se(IV)

extracted amounts vary as those of total Se. The first extraction procedure solubilizes a large part of Se(IV) which represents 50% of the total extracted Se. With the repetition of extractions, the Se(IV) extracted amounts decrease. However, Se(IV) is present in all the solubilized fractions and, from the second extraction step, Se(IV) represents approx. 30% of total Se in each extract.

The high proportion of Se(IV) in the first extraction step can be mainly assigned to the high capacity of immobilization of this Se form on iron, manganese or aluminium oxyhydroxides (Barrow, 1992; Masscheleyn and Patrick, 1993; Tam et al., 1995) and humic substances (Gustafsson and Johnsson, 1994; Tam et al., 1995). The use of an extraction solution with pH > 8 allows then to solubilize adsorbed Se(IV). On the other hand, the important presence of Se(IV) in the following extracts can confirm the hypothesis of a slow oxidation of the reduced forms of Se into Se(IV).

3.2.2. Selenium speciation method

Independent 20 μg l^{-1} solutions of Se(IV), Se(VI), selenomethionine and selenocystine have been prepared in 2 mol l^{-1} sodium hydroxide and submitted to a 3-h sonication period in order to evaluate the stability of these Se species during a single alkaline extraction procedure. The conservation study of elemental Se and inorganic Se(−II) in this medium has not been performed

Table 3
Stability of different Se compounds in alkaline solution (20 μg l^{-1}) during a single step extraction procedure

Se solutions	[Se(IV)] (μg l^{-1}) $\pm \sigma_n$ ($n = 3$)	[Se(VI)] (μg l^{-1}) $\pm \sigma_n$ ($n = 3$)	[Total Se] (μg l^{-1}) $\pm \sigma_n$ ($n = 3$)
Se(IV)	20.1 ± 0.2	n.d.	19.8 ± 0.8
Se(VI)	n.d.	19.9 ± 1.0	20.4 ± 0.6
Selenomethionine	n.d.	n.d.	19.5 ± 0.9
Selenocystine	4.6 ± 0.3	n.d.	20.1 ± 0.2

Note: n.d., non-detected.

because these Se compounds are not commercially available with a suprapure quality. The total Se, Se(IV) and Se(VI) concentrations have been determined in each solution; these values are given in Table 3.

Results show no detectable oxidation of selenite to selenate over the 3-h procedure. Niss et al. (1993) also found a quantitative recovery of these Se forms from spiked fly ash submitted to an alkaline extraction (4 h) in an ultrasonic bath. Selenomethionine does not seem to be affected by the extraction procedure because no transformation into Se(IV) or Se(VI) has been found. On the other hand, selenocystine is oxidized to Se(IV) with an efficiency of 23%.

Because of this last result concerning selenocystine and a possible oxidation of the different Se species with the repeated extractions, the following speciation study is only applied to the first step of the extraction procedure in order to minimize the oxidation of the reduced Se species.

The speciation schema of soil Se applied is illustrated in Fig. 3 which is based upon the fractionation of humic substances as a function of their solubility in acidic or basic solutions.

Three groups of molecules can be separated: humic acids (HA) only soluble in basic solutions; fulvic acids (FA) soluble both in acidic and alkaline media; and humins which are the non-soluble fraction (Chamayou and Legros, 1989).

The results obtained by the application of the selenium speciation schema to the studied soil are given in Fig. 4.

Seventy percent of the total selenium dissolved by one-step alkaline extraction are found in the acid-soluble fraction while 30% precipitates in the non-acid-soluble fraction.
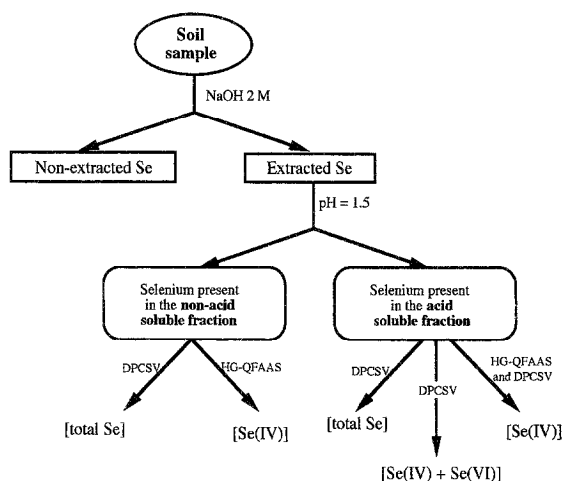
Fig. 3. Speciation schema of selenium in soil.

3.2.2.1. Forms of Se in the acid-soluble fraction (FA).

In this fraction, the Se(IV) concentration has been measured by the two analytical methods as organic matter strongly disturbs the Se(IV) determinations by DPCSV, an optimization of the analytical procedure in presence of fulvic acids was necessary (Potin Gautier et al., 1994).

Results of Se(IV) determinations (Fig. 4) performed by both DPCSV and HG-QFAAS are in excellent agreement, DPCSV giving a much better reproducibility.

The Se(VI) concentration has been determined by DPCSV after reduction into Se(IV). The difference between mean concentration values of the sum [Se(IV) + Se(VI)] and total Se of this fraction can be assumed to represent the concentration of selenium which is organically bound. These compounds could correspond to seleno–amino acids such as selenomethionine, identified by Abrams et al. in soil samples (Abrams

Fig. 4. Se concentration values obtained after the speciation study (expressed in μg Se g^{-1} dry soil).

Se(IV) determination has never been performed in the humic-acid fraction precipitated at acid pH. Only the total amount of Se is usually determined and selenium is therefore assumed to be essentially present in the form of seleno–amino acids (Yamada and Hattori, 1990; Gustafsson and Johnsson, 1992). However, from the results presented in Fig. 4, it is probable that Se is not totally present in the Se(IV) form part can result in an oxidation of organic Se($-$II) to Se(IV) occurring during the whole treatment.

The selenate concentration has not been determined because the necessary reduction of Se(VI) into Se(IV) should be performed in a hydrochloric acid solution at a pH where humic acids precipitate and make uncertain the Se(VI) reduction.

The pH and redox potential factors have a great influence on the distribution and availability of selenium in soils (Elrashidi et al., 1989; Masscheleyn et al., 1990; Masscheleyn and Patrick, 1993; Jayaweera and Biggar, 1996; Tokunaga et al., 1996; Zawislanski and Zavarin, 1996). (Masscheleyn et al., 1990; Masscheleyn and Patrick, 1993) and Elrashidi et al. (1989) have shown that Se(IV) prevails for neutral soils with a moderated redox potential. As the pH of the studied soil is neutral, it seems expected that Se(IV) represents the main Se form [Se(IV) represents, respectively, 44%, 60% and 51% of the acid-soluble, non-acid-soluble fractions and the alkaline extraction]. The sum of the Se(IV) concentrations determined in the two fractions (HA and FA) (1.35 $\pm$ 0.05 μg Se g^{-1}) is not strictly identical to the total soluble Se(IV) concentration (1.50 $\pm$ 0.03 μg Se g^{-1}), but the difference is not highly significant owing to analytical difficulties involved.

3.2.2.3. Reproducibility of the speciation method. Reproducibility has been evaluated by means of calculation of the relative standard deviation (% R.S.D.) from three measurements on three independent treatments of soil sample.

The highest R.S.D. values have been obtained for the total Se determinations in the acid-soluble fraction (5%) and for the non-acid-soluble fraction (13%) because of the large number of sample treatment steps before analysis. On the other

and Burau, 1989; Abrams et al., 1990) or peptides and proteins because the Se(0) and Se($-$II) inorganic forms are strongly fixed in soils and are insoluble in sodium hydroxide (Elrashidi et al., 1989; Masscheleyn et al., 1990).

The balance sheet of the selenium forms' distribution in the acid-soluble fraction (Fig. 4) shows that the main Se form is Se(IV) and Se(VI) is a minor component. Although an organic Se($-$II) transformation into Se(IV) may be possible, this fraction contains significant amounts of organic Se. A recent study has shown that organic Se compounds as selenomethionine or selenourea can be immobilized on iron oxyhydroxide and an increase of pH to pH 6 results in a release of these forms (Tam et al., 1995).

3.2.2.2. Forms of Se in the non-acid-soluble fraction (HA). In this fraction, the Se(IV) concentration has been determined only by HG-QFAAS after dissolution of the precipitate in 2 mol l^{-1} NaOH. DPCSV cannot be used to evaluate Se(IV) because an emulsion is produced during the nitrogen purge, preventing measurements. From the results of Fig. 4, Se(IV) represents approx. 60% of total extracted Se. To our knowledge, direct

hand, reproducibilities corresponding to direct Se(IV) determination (from 1 to 2%) or the [Se(IV) + Se(VI)] sum (4.8%) are satisfactory.

Resins have often been used in the literature to remove organic matter from soil extracts (Abrams and Burau, 1989; Fio and Fujii, 1990; Kang et al., 1993). The optimization of the analytical methods for the determination of Se(IV) in presence of humic substances (Lespes et al., 1994; Potin Gautier et al., 1994) has allowed us to establish this speciation schema without using resins, minimizing Se losses.

4. Conclusion

The speciation schema developed in this study has evaluated the Se species distribution in a soil. First, the water-soluble fraction has been extracted from the soil. The total selenium concentration recovered is low ($2.0 \pm 0.1\%$) and the speciation analysis have shown that only Se(IV) and Se(VI) are present in this water-soluble extract and Se(VI) is in the majority.

In order to obtain more information on the Se distribution in this Irish soil, an alkaline extraction has been applied and has facilitated a higher recovery ($50 \pm 1\%$). Then, the alkaline extract is acidified (pH 1.5) to separate the acid-soluble fraction (FA) from the solid fraction at this pH (HA). The two fractions contain selenium and the richer is the acid-soluble fraction. Results of the speciation analysis indicate that Se(IV) is the main Se form. Se(VI) represents only 15% of the total extracted Se in the acid-soluble fraction but this form cannot be determined in the other fraction.

Unidentified forms of selenium are present in large amounts in the studied soil, probably in the form of Se organic compounds. Their behaviour in soil are mostly unknown so it would be interesting to obtain such information for a better understanding of Se availability.

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♣EPA Ground Water Issue

Behavior of Metals in Soils

Joan E. McLean* and Bert E. Bledsoe**

The Regional Superfund Ground-Water Forum is a group of scientists, representing EPA's Regional Superfund Offices, organized to exchange up-to-date information related to ground-water remediation at Superfund sites. One of the major issues of concern to the Forum is the mobility of metals in soils as related to subsurface remediation.

For the purposes of this Issue Paper, those metals most commonly found at Superfund sites will be discussed in terms of the processes affecting their behavior in soils as well as laboratory methods available to evaluate this behavior. The retention capacity of soil will also be discussed in terms of the movement of metals between the other environmental compartments including ground water, surface water, or the atmosphere. Long-term changes in soil environmental conditions, due to the effects of remediation systems or to natural weathering processes, are also discussed with respect to the enhanced mobility of metals in soils.

For further information contact Bert Bledsoe (405) 332-8800 or FTS 700-743-2324 at RSKERL-Ada.

Introduction

The purpose of this document is to introduce to the reader the fundamental processes that control the mobility of metals in the soil environment. This discussion will emphasize the basic chemistry of metals in soils and will provide information on laboratory methods used to evaluate the behavior of metals in soils. The metals selected for discussion in this document are the metals most commonly found at Superfund sites and will be limited to lead (Pb), chromium (Cr), arsenic (As), cadmium (Cd), nickel (Ni), zinc (Zn), copper (Cu), mercury (Hg), silver (Ag), and selenium (Se).

Metals are defined as any element that has a silvery luster and is a good conductor of heat and electricity. There are many terms used to describe and categorize metals, including trace metals, transition metals, micronutrients, toxic metals, heavy metals. Many of these definitions are arbitrary and these terms have been used loosely in the literature to include elements that do not strictly meet the definition of the term. Strictly speaking arsenic and selenium are not metals but are metalloids, displaying both metallic and non-metallic properties. For this paper, the term metal will be used to include all the elements under discussion.

The average concentration of select metals in soils is listed in Table 1. All soils naturally contain trace levels of metals. The presence of metals in soil is, therefore, not indicative of contamination. The concentration of metals in uncontaminated soil is primarily related to the geology of the parent material from which the soil was formed. Depending on the local geology, the concentration of metals in a soil may exceed the ranges listed in Table 1. For example, Se concentration in non-seleniferous soils in the U.S. range from 0.1 to 2 mg/Kg. In seleniferous soils, Se ranges from 1 to 80 mg/Kg, with reports of up to 1200 mg/Kg Se (McNeal and Balistrier, 1989). Use of common ranges or average concentration of trace metals in soils as an indicator of whether a soil is contaminated is not appropriate since the native concentration of metals in a specific soil may fall out of the listed ranges. Only by direct analysis of uncontaminated soils can background levels of metals be determined.

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Table 1. Content of Various Elements in Soils (Lindsay, 1979)

Metal	Selected Average for Soils mg/kg	Common Range for Soils mg/kg
Al	71,000	10,000-300,000
Fe	38,000	7,000-550,000
Mn	600	20-3,000
Cu	30	2-100
Cr	100	1-1000
Cd	0.06	0.01-0.70
Zn	50	10-300
As	5	1.0-50
Se	0.3	0.1-2
Ni	40	5-500
Ag	0.05	0.01-5
Pb	10	2-200
Hg	0.03	0.01-0.3

Metals associated with the aqueous phase of soils are subject to movement with soil water, and may be transported through the vadose zone to ground water. Metals, unlike the hazardous organics, cannot be degraded. Some metals, such as Cr, As, Se, and Hg, can be transformed to other oxidation states in soil, reducing their mobility and toxicity.

Immobilization of metals, by mechanisms of adsorption and precipitation, will prevent movement of the metals to ground water. Metal-soil interaction is such that when metals are introduced at the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded, or metal interaction with the associated waste matrix enhances mobility. Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix in question.

Fate of Metals in the Soil Environment

In soil, metals are found in one or more of several "pools" of the soil, as described by Shuman (1991):

1) dissolved in the soil solution;
2) occupying exchange sites on inorganic soil constituents;
3) specifically adsorbed on inorganic soil constituents;
4) associated with insoluble soil organic matter;
5) precipitated as pure or mixed solids;
6) present in the structure of secondary minerals; and/or
7) present in the structure of primary minerals.

In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. The aqueous fraction, and those fractions in equilibrium with this fraction, i.e., the exchange fraction, are of primary

importance when considering the migration potential of metals associated with soils.

Multiphase equilibria must be considered when defining metal behavior in soils (Figure 1). Metals in the soil solution are subject to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization, a potentially important mechanism for Hg, Se, and As. At the same time metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation-reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions. The ability to predict the concentration of a given metal in the soil solution depends on the accuracy with which the multiphase equilibria can be determined or calculated.

Most studies of the behavior of metals in soils have been carried out under equilibrium conditions. Equilibrium data indicate which reactions are likely to occur under prescribed conditions, but do not indicate the time period involved. The kinetic aspect of oxidation/reduction, precipitation/dissolution, and adsorption/desorption reactions involving metals in soil matrix suffers from a lack of published data. Thus the kinetic component, which in many cases is critical to predict the behavior of metals in soils, cannot be assessed easily. Without the kinetic component, the current accepted approach is to assume that local equilibrium occurs in the soil profile. Equilibrium thermodynamic data can then be applied not only to predict which precipitation/dissolution, adsorption/desorption, and/or oxidation/reduction reactions are likely to occur under a given set of conditions, but also to estimate the solution composition, i.e., metal concentration in solution, at equilibrium. This approach relies heavily on the accuracy of thermodynamic data that can be found in the literature.

Soil Solution Chemistry

Metals exist in the soil solution as either free (uncomplexed) metal ions (e.g., Cd^{2+}, Zn^{2+}, Cr^{3+}), in various soluble complexes with inorganic or organic ligands (e.g., $CdSO_4^o$, $ZnCl^+$, $CdCl_3^-$), or associated with mobile inorganic and organic colloidal material. A complex is defined as an unit in which a central metal ion is bonded by a number of associated atoms or molecules in a defined geometric pattern, e.g $ZnSO_4^o$, $CdHCO_3^+$, $Cr(OH)_4^-$. The associated atoms or molecules are termed ligands. In the above examples, SO_4^{2-}, HCO_3^-, and OH^- are ligand. The total concentration of a metal, Me_T, in the soil solution is the sum of the free ion concentration $[Me^{z+}]$, the concentration of soluble organic and inorganic metal complexes, and the concentration of metals associated with mobile colloidal material.

Metals will form soluble complexes with inorganic and organic ligands. Common inorganic ligands are SO_4^{2-}, Cl^-, OH^-, PO_4^{3-}, NO_3^- and CO_3^{2-}. Soil organic ligands include low molecular weight aliphatic, aromatic, and amino acids and soluble constituents of fulvic acids. Formation constants for various metal complexes are available in the literature (e.g., see Nordstrom and Munoz, 1985; Lindsay, 1979; Martell and Smith, 1974 -1982). Organic complexation of metals in soil is not as well defined as inorganic complexation because of the difficultly of identifying the large number of organic ligands that
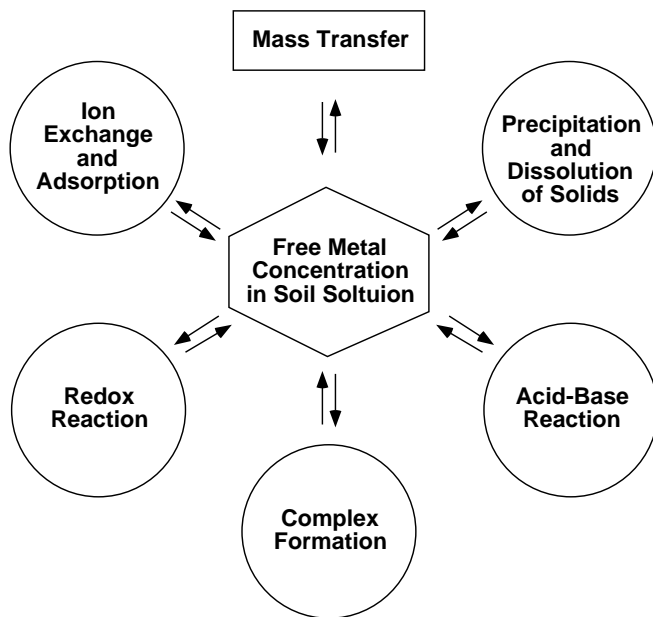
Figure 1. Principal controls on free trace metal concentrations in soils solution (Mattigod, et al., 1981).

may be present in soils. Most of the metal-organic complex species identified in the literature were generated from metal interaction with fulvic acids extracted from sewage sludges (Baham, et al., 1978; Baham and Sposito, 1986; Behel, et al., 1983; Boyd et al., 1979; Boyd et al., 1983; Dudley, et al., 1987; Lake et al., 1984; Sposito et al., 1979; Sposito et al., 1981; Sposito et al., 1982). The soluble metal organic complexes that may form in other waste systems, however, have not been identified.

The presence of complex species in the soil solution can significantly affect the transport of metals through the soil matrix relative to the free metal ion. With complexation, the resulting metal species may be positively or negatively charged or be electrically neutral (e.g., $CdCl_3^+$, $CdCl^-$, $CdCl_2^o$). The metal complex may be only weakly adsorbed or more strongly adsorbed to soil surfaces relative to the free metal ion. A more detailed discussion on the effect complex formation has on metal mobility is given in the section: Effect of anions on adsorption and precipitation. Speciation not only affects mobility of metals but also the bioavailability and toxicity of the metal. The free metal ion is, in general, the most bioavailable and toxic form of the metal.

Several metals of environmental concern exist in soils in more than one oxidation state: arsenic, As(V) and As(III), selenium, Se(VI) and Se(IV), chromium, Cr(VI) and Cr(III), and mercury, Hg(II) and Hg(I). The oxidation state of these metals determines their relative mobility, bioavailability, and toxicity. For example, hexavalent Cr is relatively mobile in soils, being only weakly sorbed by soils. Hexavalent Cr is also extremely toxic and a known carcinogen. Trivalent Cr, on the other hand, is relatively immobile in soil, being strongly sorbed by soils and readily forming insoluble precipitates, and it is of low toxicity.

Atomic absorption spectrophotometers (AA) and inductively coupled plasma emission spectrometers (ICP) are commonly used to determine the metal concentration in soil solutions. Both techniques measure the total metal concentration in the solution without distinguishing metal speciation or oxidation state. Free metal, complexed metal ion concentrations and concentration of metals in different oxidation states can be determined using ion selective electrodes, polarography, colorimetric procedures, gas chromatography-AA, and high performance liquid chromatography-AA (see Kramer and Allen, 1988). While these specific methods are necessary for accurate measurements of metal speciation and oxidation state, these methods are not routinely performed by commercial laboratories nor are these procedure standard EPA methods.

Metal concentrations determined by AA or ICP are often used as inputs into a thermodynamic computer program, such as MINTEQA2 (USEPA, 1987). This program can be used to calculate the speciation and oxidation state of metals in soil solution of known composition. Formation constants are known for many metal complexes. There is, however, only limited information for metal-organic complexes, including formation constants for many naturally occurring ligands and those in waste disposal systems. The required input data for these models include: the concentration of the metal of interest, the inorganic and organic ligands, and the major cations and other metal ions, and pH. In specific cases the redox potential and pCO_2 also may be required. Output consists of an estimation of the concentration of free metals and complexed metals at equilibrium for the specified conditions.

Many predictive methods, based on solution and solid phase chemistry, do not adequately describe transport of metals under field conditions. Solution chemistry considers the interaction between dissolved species, dissolved being defined as substances that will pass a 0.45µm filter. However, in addition to dissolved metal complexes, metals also may associate with mobile colloidal particles. Colloidal size particles are particles with a diameter ranging from 0.01 and 10µm (Sposito, 1989). Gschwend and Reynolds (1987) reported that colloidal particles of intermediate diameter, 0.1µm to 1µm, were the most mobile particles in a sandy medium. Colloidal particles include iron and manganese oxides, clay minerals, and organic matter. These surfaces have a high capacity for metal sorption. Puls et al. (1991) reported a 21 times increase in arsenate transport in the presence of colloidal material compared with dissolved arsenate. This increased transport of contaminants associated with mobile colloidal material has been termed facilitated transport.

Solid Phase Formation

Metals may precipitate to form a three dimensional solid phase in soils. These precipitates may be pure solids (e.g., $CdCO_3$, $Pb(OH)_2$, ZnS_2) or mixed solids (e.g., $(Fe_xCr_{1-x})(OH)_3$, $Ba(CrO_4,SO_4)$). Mixed solids are formed when various elements co-precipitate. There are several types of co-precipitation, inclusion, adsorption and solid solution formation, distinguished by the type of association between the trace element and the host mineral (Sposito, 1989). Solid solution formation occurs when the trace metal is compatible

3

with the element of the host mineral and thus can uniformly replace the host element throughout the mineral. An example of solid solution formation is the substitution of Cd for Ca in calcium carbonate. Cadmium and Ca have almost identical ionic radii so that Cd can readily substitute of Ca in this carbonate mineral. Mechanisms of retention, whether surface adsorption, surface precipitation, co-precipitation, and pure solid formation are often difficult to distinguish experimentally. Retention involves a progression of these processes. The term sorption is used when the actual mechanism of metal removal from the soil solution is not known.

Stability diagrams are used as a convenient technique for illustrating how the solubility of metal compounds varies with soil pH and with metal concentration (or activity). The diagrams also allow some prediction of which solid phase regulates metal activity in the soil solution. Methods for constructing such diagrams is given in Sposito (1989) and Lindsay (1979). Santillan-Medrano and Jurinak (1975) used stability diagrams for predicting the formation of precipitates of Pb and Cd in a calcareous soil. The stability diagrams (Figures 2 and 3) illustrate the decrease in Pb and Cd solubility with increasing pH, which is the usual trend with cationic metals. Solution activity of Cd is consistently higher than that for Pb indicating that Cd may be more mobile in the environment. Lead phosphate compounds at lower pH and a mixed Pb compound at pH>7.5 could be the solid phases regulating Pb in solution. The authors concluded that cadmium solution activity is regulated by the formation of $CdCO_3$ and $Cd(PO_4)_2$ or a mixed Cd solid at pH<7.5. At higher pH, the system is undersaturated with respect to the Cd compounds considered.

The formation of a solid phase may not be an important mechanism compared to adsorption in native soils because of the low concentration of trace metals in these systems (Lindsay, 1979). Precipitation reactions may be of much greater importance in waste systems where the concentration of metals may be exceedingly high. McBride (1980)
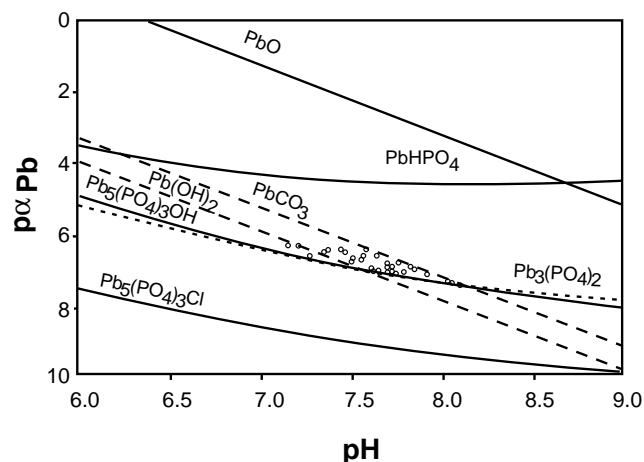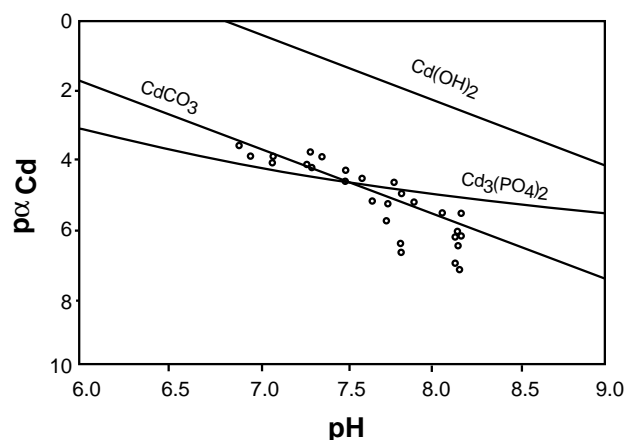
Figure 3. The solubility diagram for Cd in Nibley clay loam soil (Santillan-Medrano and Jurinak, 1975).

concluded that calcite ($CaCO_3$) serves as a site for adsorption of Cd^{2+} at low concentrations of Cd, while $CdCO_3$ precipitation, possibly as a coating on the calcite, occurs only at higher Cd concentrations.

Surface Reactions

Adsorption is defined as the accumulation of ions at the interface between a solid phase and an aqueous phase. Adsorption differs from precipitation in that the metal does not form a new three dimensional solid phase but is instead associated with the surfaces of existing soil particles. The soil matrix often includes organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates, and amorphous aluminosilicates.

Soil organic matter consists of 1) living organisms, 2) soluble biochemicals (amino acids, proteins, carbohydrates, organic acids, polysaccharides, lignin, etc.), and 3) insoluble humic substances. The biochemicals and humic substances provide sites (acid functional groups, such as such as carboxylic, phenolics, alcoholic, enolic-OH and amino groups) for metal sorption. A discussion of the nature of soil organic matter and its role in the retention of metals in soil is given by Stevenson (1991) and Stevenson and Fitch (1990). The biochemicals form water soluble complexes with metals, increasing metal mobility, as discussed in a previous section. The humic substances consists of insoluble polymers of aliphatic and aromatic substances produced through microbial action. Humic substances contain a highly complex mixture of functional groups. Binding of metals to organic matter involves a continuum of reactive sites, ranging from weak forces of attraction to formation of strong chemical bonds. Soil organic matter can be the main source of soil cation exchange capacity, contributing >200meq/100 g of organic matter in surface mineral soils. Organic matter content, however, decreases with depth, so that the mineral constituents of soil will become a more important surface for sorption as the organic matter content of the soil diminishes.

There have been numerous studies of the adsorptive properties of clay minerals, in particular montmorillonite and

Figure 2. The solubility diagram for Pb in Nibley clay loam soil (Santillan-Medrano and Jurinak, 1975).

kaolinite, and iron and manganese oxides. Jenne (1968) concluded that Fe and Mn oxides are the principal soil surface that control the mobility of metals in soils and natural water. In arid soils, carbonate minerals may immobilize metals by providing an adsorbing and nucleating surface (Santillan-Medrano and Jurinak, 1975; Cavallaro and McBride, 1978; McBride, 1980; Jurinak and Bauer, 1956; McBride and Bouldin, 1984; Dudley et al., 1988; Dudley et al., 1991).

Soil surfaces carry either a net negative or positive charge depending on the nature of the surface and the soil pH. The permanent net negative charge on surfaces is due to charge imbalance resulting from the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layers and/or substitution of Mg^{2+}, Fe^{2+}, etc. for Al^{3+} in the octahedral layers of aluminosilicate clays. The charge on the surface is not affected by changes in soil pH and hence it is termed a permanent charged surface. pH dependent charged surfaces are associated with the edges of clay minerals, with the surfaces of oxides, hydroxides and carbonates, and with organic matter (acid functional groups). The charge arises from the association and dissociation of protons from surface functional groups. Using an iron oxide surface functional group as an example, the association of protons with the functional group results in a positive charge [-Fe-OH$_2^+$] and dissociation of protons, under more alkaline conditions, results in a negative charge [-Fe-O$^-$]. At the point of zero net proton charge (PZNPC) the functional group is neutral [-Fe-OH^o]. For all pH dependent charged surfaces, whether organic or inorganic, as the pH decreases, the number of negatively charged sites diminishes. Under more acidic conditions, the majority of pH dependent surfaces will be positively charged and under more alkaline conditions, the majority of sites will be negatively charged. The pH dependent charged surfaces in soils differ widely in their PZNPC.

The structural charge developed on either a permanent charged surface or a pH dependent charged surface must be balanced by ions of opposite charge at or near the surface. The cation exchange capacity is a measure of the negatively charged sites for cation adsorption and anion exchange capacity is a measure of the positively charged sites for anion adsorption. The anion capacity is, however, very small relative to the cation adsorption capacity of soils.

A surface complexation model is often used to describe adsorption behavior (Sposito, 1989). Several types of surface complexes can form between a metal and soil surface functional groups and are defined by the extent of bonding between the metal ion and the surface (Figure 4). Metals in a diffuse ion association or in an outer sphere complex are surrounded by waters of hydration and are not directly bonded to the soil surface. These ions accumulate at the interface of the charged surfaces in response to electrostatic forces. These reactions are rapid and reversible with only a weak dependence on the electron configuration of the surface group and the adsorbed ion. These two metal-surface interactions have also been termed exchange reactions because the introduction of other cations into the system, in sufficient concentration, causes the replacement or exchange of the original cations. Metals associated with exchange sites may, depending on the environment, be relatively mobile. Exchangeable metals may be the most significant reserve of potentially mobile metals in soil (Silveira and Sommers, 1977; Latterell et al., 1978).
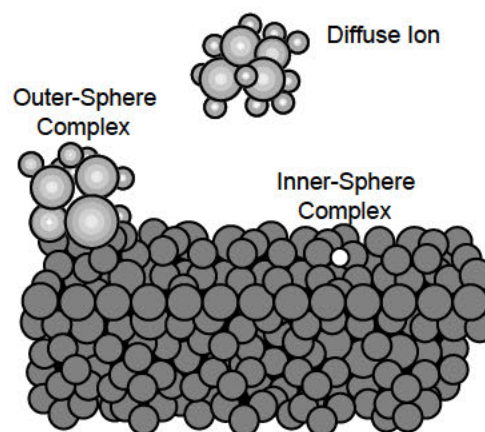
Figure 4. The three mechanisms of cation adsorption on a siloxane surface (e.g., montmorillonite). (Spositi, 1989).

With inner sphere complexation, the metal is bound directly to the soil surface, no waters of hydration are involved. It is distinguished from the exchangeable state by having ionic and/or covalent character to the binding between the metal and the surface. A much higher bonding energy is involved than in exchange reactions, and the bonding depends on the electron configuration of both the surface group and the metal. This adsorption mechanism is often termed specific adsorption. The term specific implies that there are differences in the energy of adsorption among cations, such that other ions, including major cations, Na, Ca, Mg, do not effectively compete for specific surface sites. Specifically adsorbed metal cations are relatively immobile and unaffected by high concentrations of the major cations due to large differences in their energies of adsorption.

At low concentrations, metals are adsorbed by the specific adsorption sites. These adsorbed metals are not removed by the input of major cations. With increasing concentration of the metal, the specific sites become saturated and the exchange sites are filled (Hendrickson and Corey, 1981; Lehmann and Harter, 1984; Garcia-Miragaya et al., 1986; O'Connor et al., 1984; O'Connor et al., 1983). Metals associated with these nonspecific sites are exchangeable with other metal cations and are thus potentially mobile. For example, in an adsorption study using Cd, O'Connor et al.(1984) showed two mechanisms were responsible for metal retention by soil. The authors attributed the first mechanism, active at low concentration (0.01-10mg/L added Cd), to specific adsorption. At higher concentrations (100-1000mg/L added Cd), adsorption was attributed to exchange reactions. Desorption studies showed that the added Cd at low concentration was not removed by 0.05M calcium solutions, whereas at the higher loading rates, the calcium salt removed significant amounts of the adsorbed Cd. These results indicate that the observed affinity of a metal for soil surfaces is concentration dependent. These results also emphasize the importance of using literature or laboratory generated values that cover the range of metal concentration of interest at a specific location. Use of data generated in the wrong concentration range may lead to misinterpretation of the metal binding strength of the soil.

The relative affinity of a soil surface for a free metal cation increases with the tendency of the cation to form strong bonds, i.e., inner sphere complexes, with the surface. The general order of preference for monovalent cations by montmorillonite is Cs > Rb > K = NH_4 > Na > Li. For the alkaline earth metals the order is Ba > Sr > Ca > Mg. The preference series indicates a greater attraction of the surface for the less hydrated cations that can fit closer to the clay surface. For transition metals, the size of the hydrated cation cannot be used as the only predictor of adsorption affinity since the electron configuration of a metal plays an important role in adsorption. Table 2 reports on results from various researches on the relative sorption affinity of metals onto a variety of soils and soil constituents. Although there is consistently a higher affinity of these surfaces for Pb and Cu compared with Zn or Cd, the specific order of sorption affinity depends on the properties of the metals, surface type, and experimental conditions.

Anions in the Soil Environment

Common anionic contaminants of concern include: arsenic (AsO_4^{3-} and AsO_2^{-}), selenium (SeO_3^{2-} and SeO_4^{2-}), and chromium in one of its oxidation states (CrO_4^{2-}). Soil particles, though predominantly negatively charged, also may carry some positive charges. The oxide surfaces, notably iron, manganese, and aluminum oxides, carbonate surfaces, and insoluble organic matter can generate a significant number of positive charges as the pH decreases. The edges of clay minerals also carry pH dependent charge. These edge sites may be important sites of retention of anions at pHs below the point of zero charge (PZC).

Clay minerals, oxides, and organic matter exert a strong preference for some anions in comparison to other anions, indicating the existence of chemical bonds between the surface and the specific anion. Phosphate has been the most extensively studied anion that exhibits this specific adsorption (inner sphere complex) phenomenon. Selenite (SeO_3^{2-}) and arsenate (AsO_4^{3-}) are adsorbed to oxides and soils through specific binding mechanisms (Rajan, 1979; Neal, et al., 1987b). Selenite (SeO_4^{2-}) and hexavalent chromium are only

weakly bound to soil surfaces and are thus easily displaced by other anions. Balistrieri and Chao (1987) found the sequence of adsorption of anions onto iron oxide to be: phosphate = silicate = arsenate > bicarbonate/carbonate > citrate = selenite > molybdate > oxalate > fluoride = selenate > sulfate. The adsorption capacity for anions is, however, small relative to cation adsorption capacity of soils.

Soil Properties Affecting Adsorption

The adsorption capacity (both exchange and specific adsorption) of a soil is determined by the number and kind of sites available. Adsorption of metal cations has been correlated with such soil properties as pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content. Anion adsorption has been correlated with Fe and Mn oxide content, pH, and redox potential. Adsorption processes are affected by these various soil factors, by the form of the metal added to the soil, and by the solvent introduced along with the metal. The results of these interactions may increase or decrease the movement of metals in the soil water.

Korte et al. (1976) qualitatively ranked the relative mobilities of 11 metals added to 10 soils (Table 3) to simulate movement of metals under an anaerobic landfill situation. The leachate used was generated in a septic tank, preserved under carbon dioxide and adjusted to pH of 5. Of the cationic metals studied lead and copper were the least mobile and mercury(II) was the most mobile (Figure 5). The heavier textured soils with higher pHs (Molokai, Nicholson, Mohaveca and Fanno) were effective in attenuating the metals, while sandy soils and/ or soils with low pH did not retain the metals effectively. For the anionic metals, clay soils containing oxides with low pH were relatively effective in retaining the anions (Figure 6). As with the cationic metals, the light textured soils were the least effective in retaining the anions. Chromium (VI) was the most mobile of the metals studied. Griffin and Shimp (1978) found the relative mobility of nine metals through montmorillonite and kaolinite to be: Cr(VI) > Se > As(III) > As(V) > Cd > Zn > Pb > Cu > Cr(III).

Table 2. Relative affinity of metals for soils and soil constituents

Soil or Soil Constituent	Relative Order of Sorption	Reference
goethite	Cu>Pb>Zn>Co>Cd	Forbes et al., 1976
Fe oxide	Pb>Cu>Zn>Cd	Benjamin and Leckie, 1981
montmorillonite	Cd=Zn>Ni	Puls and Bohn, 1988
kaolinite	Cd>Zn>Ni	Puls and Bohn, 1988
soils	Pb>Cu>Zn>Cd>Ni	Biddappa et al., 1981
soils	Zn>Ni>Cd	Tiller et al., 1984
mineral soils	Pb>Cu>Zn>Cd	Elliott et al., 1986
organic soils	Pb>Cu>Cd>Zn	Elliott et al., 1986
soil	Pb>Cu>Zn>Ni	Harter, 1983

Table 3. Characteristics of the soils (Korte et al., 1976)

Soil	Order	pH meq/100g	CEC m2/g	Surface Area %	Free Fe oxides %	Clay	Texture
Wagram	Ultisol	4.2	2	8.0	0.6	4	loamy sand
Ava	Alfisol	4.5	19	61.5	4	31	silty clay loam
Ka kaska	Spodosol	4.7	10	8.9	1.8	5	sand
Davidson	Ultisol	6.2	9	61.3	17	61	clay
Molokai	Oxisol	6.2	14	67.3	23	52	clay silty clay
Chalmers	Mollisol	6.6	26	125.6	3.1	35	loam
Nicholson	Alfisol	6.7	37	120.5	5.6	49	silty day
Fanno	Alfisol	7	33	122.1	3.7	46	clay
Mohave	Aridisol	7.3	10	38.3	1.7	11	sandy loam
Mohave ca	Aridisol	7.8	12	127.5	2.5	40	clay loam
Anthony	Entisol	7.8	6	19.8	1.8	15	sandy loam
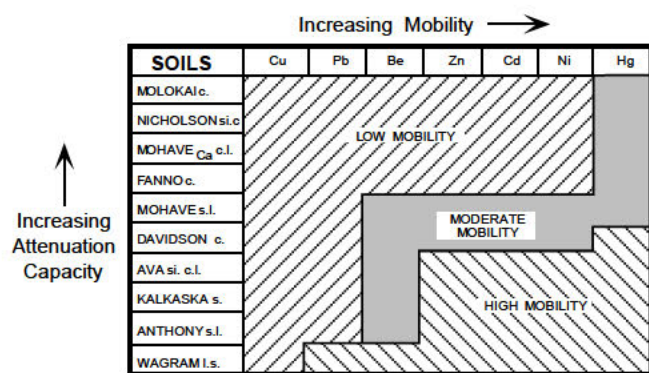
Figure 5. Relative mobility of cations through soil. (From Korte, Skopp, Fuller, Niebla, and Alesii, 1976).
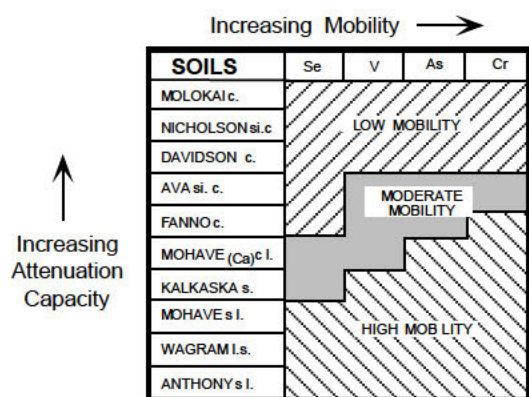
Figure 6. Relative mobility of anions through soil. (From Korte, Skopp, Fuller, Niebla, and Alesii, 1976).

Factors Affecting Adsorption and Precipitation Reactions

Although the principles affecting sorption and precipitation are similar for cationic and anionic metals, for clarity, the following section will concentrate on a general discussion of factors affecting the behavior of cationic metals in soils. Factors affecting anion adsorption and precipitation will be discussed for each individual metal anion in a later section.

Effect of competing cations

For specific adsorption sites, trace cationic metals are preferentially adsorbed over the major cations (Na, Ca, Mg) and trace anionic metals are preferentially adsorbed over major anions (SO_4^-, NO_3^-, soluble ionized organic acids). However, when the specific adsorption sites become saturated, exchange reactions dominate and competition for these sites with soil major ions becomes important. Cavallaro and McBride (1978) found that adsorption of Cu and Cd decreased in the presence of 0.01M $CaCl_2$. They attributed this decrease to competition with Ca for adsorption sites. Cadmium adsorption was more affected by the presence of Ca than Cu. The mobility of Cd may be greatly increased due to such competition. Likewise, Harter (1979) indicated the Ca in solution had a greater effect on Pb adsorption than on Cu. In another study, Harter (1992) added Cu, Ni and Co to calcium saturated soils. The presence of Ca, a common ion in soils with pH>5.6, did not affect Cu sorption but did limit the sorption of Co and Ni. The author emphasized the importance of these results in that standard management practice for metal contaminated soils is to raise the pH to 7, often using a Ca buffered system. The addition of Ca, as low as 0.01M Ca, may increase the mobility of some metals by competing for sorption sites.

Trace metals also will compete with each other for adsorption sites. Although there have been several studies on the relative adsorption affinities of trace metals by soils and soil constituents (see Table 2), these studies have compared how much of each metal, added to the soils as individual

components, was adsorbed and not whether the adsorption of one metal will interfere with that of another. Few studies have looked directly at the competitive adsorption of metals. Kuo and Baker (1980) reported that the presence of Cu interfered with the adsorption of Zn and Cd. Adsorbed Cu was not significantly affected by added Zn but the presence of Cu, at concentrations as low as 15 μg/L, completely prevented Zn adsorption in one soil with a low cation exchange capacity (Kurdi and Doner, 1983). In contrast, McBride and Blasiak (1979) found that Cu was ineffective in competing for Zn adsorption sites over a pH range of 5-7. The inability of Cu to block Zn adsorption in this study was taken as evidence that Zn and Cu were preferentially adsorbed at different sites. Simultaneous addition of Cd and Zn to Mn oxide lowered the adsorption of both metals (Zasoski and Burau, 1988).

The presence of other cations, whether major or trace metals, can significantly effect the mobility of the metal of interest. Use of data from the literature, generation of laboratory data, or use of computer models that do not reflect the complex mixture of metals specific to a site may not be useful to understand or accurately predict metal mobility.

Effect of complex formation

Metal cations form complexes with inorganic and organic ligands. The resulting association has a lower positive charge than the free metal ion, and may be uncharged or carry a net negative charge. For example, the association of cadmium with chloride results in the following series of charged and uncharged cadmium species: Cd^{2+}, $CdCl^+$, $CdCl_2^o$, $CdCl_3^-$. Benjamin and Leckie (1982) stated that the interaction between metal ions and complexing ligands may result in either a complex that is weakly adsorbed to the soil surface or in a complex that is more strongly adsorbed relative to the free metal ion. In general, the decrease in positive charge on the complexed metal reduces adsorption to a negatively charged surface. One noted exception is the preferential adsorption of hydrolyzed metals ($MeOH^+$) versus the free bivalent metal (James and Healy, 1972). The actual effect of complex formation on sorption depends on the properties of the metal of interest, the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox conditions, as is illustrated by the follow research results.

In the presence of the inorganic ligands Cl^- and SO_4^{2-}, the adsorption of Cd on soil and soil constituents was inhibited (O'Connor, et al., 1984; Hirsch et al., 1989; Egozy, 1980; Garcia-Miragaya and Page, 1976; Benjamin and Leckie, 1982) due to the formation of cadmium complexes that were not strongly adsorbed by the soils. Using much higher concentrations of salt than normally encountered in soil solutions (0.1 to 0.5M NaCl), Doner (1978) concluded that the increased mobility of Ni, Cu, and Cd through a soil column was due to complex formation of the metals with Cl^-. The mobility of Cd increased more than that of Ni and Cu, Ni being the least mobile. These observed mobilities are in the same order as that of the stability constants of the chloride complexes of these metals. Within normal concentration of electrolytes in soil solution, Elrashidi and O'Connor (1982) found no measurable change in Zn adsorption by alkaline soils due to complex formation of Zn with Cl^-, NO_3^{2-}, or SO_4^{2-} ions. Under these conditions (anion concentration of 0.1M), anion complex formation did not compete with the highly selective adsorption sites for Zn. Shuman (1986), using acid soils,

observed a decreased adsorption of Zn in the presence of Cl^- at the concentration of $CaCl_2$ used by Elrashidi and O'Connor (1982) but no effect at lower concentrations. McBride (1985), using aluminum oxide, and Cavallaro (1982), using clays, found that high levels of phosphate suppressed adsorption of Cu and Zn. Phosphate did not form strong complexes with Cu or Zn but it was strongly adsorbed to soil surfaces thus physically blocking the specific adsorption sites of Cu and Zn. Other researchers (Kuo and McNeal, 1984; Stanton and Burger, 1970; Bolland et al., 1977), using lower concentrations of added phosphate, demonstrated enhanced adsorption of Zn and Cd on oxide surfaces. At the concentration of phosphate used in these studies, the adsorption of phosphate onto the oxide surfaces increased the negative charge on the oxide surface, thus enhancing adsorption of the metal cations.

Complex formation between metals and organic ligands affects metal adsorption and hence mobility. The extent of complexation between a metal and soluble organic matter depends on the competition between the metal-binding surface sites and the soluble organic ligand for the metal. Metals that readily form stable complexes with soluble organic matter are likely to be mobile in soils. Overcash and Pal (1979) reported that the order of metal-organic complex stabilities, for the system they studied, was Hg > Cu > Ni > Pb > Co > Zn > Cd. Khan et al. (1982) showed that the mobility of metals through soil followed the order: Cu > Ni > Pb > Ag > Cd. The high mobility of Cu and Ni was attributed to their high complexing nature with soluble soil organic matter. Amrhein, et al. (1992) also showed the increased mobility of Cu, Ni, and Pb in the presence of dissolved organic matter. In this study, the Cd leached from the columns was not associated with dissolved organic carbon but was associated with Cl or acetate anions. Metals, such as Cd and Zn, that do not form highly stable complexes with organic matter are not as greatly affected by the presence of dissolved organic matter in the soil solution as metals that do form stable complexes, such as Cu, Pb, or Hg. Dunnivant et al. (1992) and Neal and Sposito (1986), however, demonstrated that dissolved organic matter does reduce Cd sorption due to complexation formation under their experimental conditions.

In systems where the organic ligand adsorbs to the soil surface, metal adsorption may be enhanced by the complexation of the metal to the surface-adsorbed ligand. Haas and Horowitz (1986) found that, in some cases, the presence of organic matter enhanced Cd adsorption by kaolinite. They interpreted these findings to suggest that the presence of an adsorbed layer of organic matter on the clay surface served as a site for Cd retention. Davis and Leckie (1978) found Cu adsorption to iron oxide increased in the presence of glutamic acid and 2,3 pyrazinendicarboxylic acid (2,3 PDCA) but decreased in the presence of picolinic acid. Picolinic acid complexed Cu and the resulting complex was not adsorbed by the oxide surface. The glutamic acid and 2,3 PDCA were adsorbed to the oxide surface, then complexed the added Cu. Using natural organic matter, Davis (1984) demonstrated the adsorption of Cu but not Cd to an organic coated aluminum oxide.

The effect of complexation formation on sorption is dependent on the type and amount of metal present, the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox. The presence of complexing ligands may increase metal retention or greatly increase metal

mobility. Use of literature or laboratory data that do not include the presence of complexing ligands, both organic and inorganic, present at the particular site of interest, may lead to significant overestimation or underestimation of metal mobility.

Effect of pH

The pH, either directly or indirectly, affects several mechanisms of metal retention by soils. Figure 7 shows the impact of soil pH on the adsorption of Pb, Ni, Zn, and Cu by two soils adjusted to various pHs ranging from approximately 4.3 to 8.3 (Harter, 1983). As is true for all cationic metals, adsorption increased with pH. The author, however, points out that the retention of the metals did not significantly increase until the pH was greater than 7. Figure 8 illustrates the adsorption of selenite, SeO_3^{2-}, on five soils adjusted to various pHs. As is true with all oxyanions, i.e., arsenic, selenium and hexavalent chromium, sorption decreases with pH.

The pH dependence of adsorption reactions of cationic metals is due, in part, to the preferential adsorption of the hydrolyzed metal species in comparison to the free metal ion (McBride, 1977; McLauren and Crawford, 1973; Davis and Leckie, 1978; Farrah and Pickering, 1976a,b; James and Healy, 1972; McBride, 1982; Cavallaro and McBride, 1980; Harter, 1983). The proportion of hydrolyzed metal species increases with pH.

Figure 8. Selenite adsorption envelope for five alluvial soils. The intitial total selenite concentration was approximately 2 $\mu mol\ kg^{-1}$ (Neal, et al., 1987a).

Figure 7. Effect of soil pH level on maximum Pb, Cu, Zn, and Ni retention by Dekalb and Hagerstown A and B horizons. Ni1 and Ni2 refer to two apparent sorption maxima. (Harter, 1983).

Cavallaro and McBride (1980) found that copper adsorption by soils showed a stronger pH dependence than Cd. This finding is consistent with the hypothesis that hydrolysis of Cu at pH 6 increases its retention by soil, while cadmium does not hydrolyze until pH 8. Zinc was shown to be retained in an exchangeable form at low pH in four Fe and Mn oxide dominated soils but became nonexchangeable as the pH was increased above 5.5 (Stahl and James, 1991). The researchers attributed this change in mechanism of sorption as being due to the hydrolysis of Zn and the adsorption of the hydrolysis species by the oxide surfaces.

Many adsorption sites in soils are pH dependent, i.e., Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals. As the pH decreases, the number of negative sites for cation adsorption diminishes while the number of sites for anion adsorption increases. Also as the pH becomes more acidic, metal cations also face competition for available permanent charged sites by Al^{3+} and H^+.

All trace metal hydroxide, oxide, carbonate, and phosphate precipitates form only under alkaline conditions (Lindsay, 1979). The dissolution of these metal precipitates is strongly dependent on the pH of the system. Jenne (1968) stated that hydrous oxides of Fe and Mn play a principal role in the retention of metals in soils. Solubility of Fe and Mn oxides is also pH-related. Below pH 6, the oxides of Fe and Mn dissolve, releasing adsorbed metal ions to solution (Essen and El Bassam, 1981).

Work by McBride and Blasiak (1979) showed increased retention of Zn with increasing pH, as is usual for metal cations. When the pH was increased above 7.5, however, the solution concentration of Zn increased. This phenomena has been observed in other studies when acid soils were adjusted to pH>7 (Kuo and Baker, 1980) and it has been attributed to

the solubilization of organic complexing ligands which effectively compete with the soil surfaces for the metal cation. Most functional groups of complexing ligands are weak acids, thus the stability of the metal complex is pH-dependent with little association in acid media. The degree of association increases with pH. Baham and Sposito (1986) and Inskeep and Baham (1983) demonstrated that the adsorption of Cu to montmorillonite, in the presence of water soluble ligands extracted from sludges and various other organic materials, decreased with increasing pH. This behavior is the opposite of the typical relationship between metal adsorption and pH. Figure 9, taken from Baham and Sposito (1986), illustrates that nearly 100% of the Cu added to the clay in the absence of the organic ligands was removed from solution at pH>7. In the presence of the organic ligands, the maximum amount of Cu removed from solution was at pH³5.5. As the pH was increased above 5.5, adsorption of Cu decreased. The explanation for this phenomena is that at low pH, H+ competes with the Cu for complexation with the organic matter. As the pH increases, more of the Cu can be complexed with the organic matter and less is therefore adsorbed by the clay. This phenomena has important implications with regards to the practice of liming acid soils to raise the pH increasing metal retention. In soils with significant levels of dissolved organic matter, increasing soil pH may actually mobilize metal due to complex formation.

The pH of the soil system is a very important parameter, directly influencing sorption/desorption, precipitation/ dissolution, complex formation, and oxidation-reduction reactions. In general, maximum retention of cationic metals occurs at pH>7 and maximum retention of anionic metals occurs at pH<7. Because of the complexity of the soil-waste system, with its myriad of surface types and solution composition, such a generalization may not hold true. For example, cationic metal mobility has been observed to increase with increasing pH due to the formation of metal complexes with dissolved organic matter.
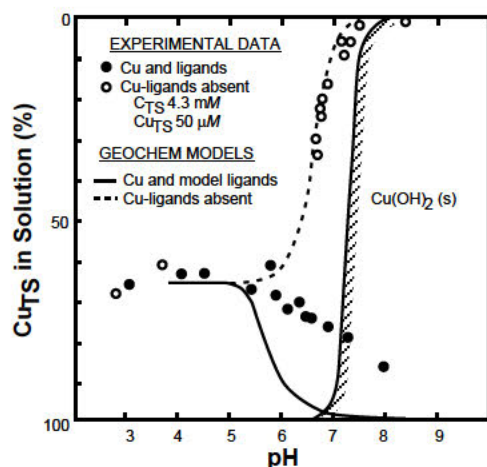
Figure 9. Adsorption of Cu [50 mmol m-3 (50 mM)] by Na-montmorillonite in the presence and absence of water soluble extract of sewage sludge (WSE). GEOCHEM simulations were constructed employing the "mixture model" (Baham and Sposito, 1986).

Effect of oxidation-reduction

Almost half of the metals under consideration have more than one oxidation state in the soil environment and are directly affected by changes in the oxidation-reduction (redox) potential of the soil. The redox potential of a soil system is the measure of the electrochemical potential or availability of electrons within a system. A chemical reaction in which an electron transfer takes place is called an oxidation-reduction process. Metals or elements which gain electrons and lose in valence are undergoing reduction, while those losing electrons and gaining in valence are becoming oxidized. A measure of the redox potential (electron availability) indicates whether the metals are in an oxidize or reduced state.

In soils, reducing conditions are brought about by the absence of oxygen (anaerobic). This is caused by the oxygen being utilized or consumed at a greater rate that it can be transported into the soil system. This can be caused by water-logged soils or soils contaminated with oxygen consuming compounds. The consumption could either be chemical or biological. The biological consumption of oxygen is the results of microbes utilizing the organic contaminant which have entered the soil system. Oxidizing conditions (aerobic) are normally found in well-drained soils as well as soils that have not been subjected to contamination by spills or leaks.

The degree of oxidation or reduction is indicated by the redox potential measurement. The four general ranges of redox conditions as suggested by Patrick and Mahapatra (1968) which may be encountered in soils are at pH 7, oxidized soils > +400 millivolts (mv); moderately reduced soils, from +400 to +100 mv; reduced soils, from +100 to -100 mv; highly reduced soils, -100 to -300 mv. The redox state of a soil, as discussed above, usually is closely related to the microbial activity and the type of substrate available to the organisms.

Redox reactions can greatly affect contaminant transport, in slightly acidic to alkaline environments, Fe(III) precipitates as a highly adsorptive solid phase (ferric hydroxide), while Fe(II) is very soluble and does not retain other metals. The reduction of Fe(III) to Fe(II) will bring about the release of ferrous iron to the pore waters and also any metals that were adsorbed to the ferric hydroxide surfaces. The behavior of chromium and selenium also illustrates the importance of redox conditions to metals movement in soils. Hexavalent Cr(VI) is both toxic and a relatively mobile anion while trivalent Cr(III) is far less toxic, relatively insoluble, and strongly adsorbs to surfaces. Selenate (Se(VI) is mobile, but less toxic than selenite (Se(IV) which is more toxic, but less mobile. In general, oxidizing conditions favor retention of metals in soils, while reducing conditions contribute to accelerated migration.

Effect of co-waste

Most soil-metal interaction studies have been performed using a specific, well characterized background solution, such as an inorganic salt solution (0.01M $CaCl_2$, Na_2SO_4, etc.) or a water soluble extraction of organic matter (leaf litter, sewage sludges, etc.). These studies, as reported above, have led to an understanding of the effects that metal type, metal concentration, solution composition, and soil surface type have on the retention of metals by soils. The behavior of metals associated with various industrial or mining wastes in

soil systems has not been extensively studied, however. In such wastes the metal concentration may be much greater than used in studies of native metals and metals associated with the controlled application of fertilizers and sewage sludges, and may be associated with a myriad of inorganic and organic chemicals that have not been characterized but may have a great effect on predicting metal mobility. Below are examples in which investigators have used various waste mixture for the background solution in sorption studies. In all cases, the results were highly dependent on the waste type used. These examples have been included to emphasize the importance of performing laboratory studies or using literature data that mimic the actual matrix of the waste or soils-waste system being investigated.

The retention of Cd, Cu, and Zn by two calcareous soils using a water extract of an acidic milling waste as the background solution (pH=4.0, dominant major cation was Ca and anion was sulfate) was studied by Dudley et al. (1988, 1991). The presence of carbonate minerals is known to effectively immobilize Cd and Cu by providing an adsorbing or nucleating surface and by buffering pH (Santillan-Medrano and Jurinak, 1975; Cavallaro and McBride, 1978; McBride and Bouldin, 1984). For the soil with a lower carbonate content (0.2% $CaCO_3$), the sorption of Cd and Zn was slow to reach equilibrium (114 hours) due to the complex set of reactions that occurred when the soil (pH 8.6) and acid milling extract (pH 4.0) were combined. The dissolution of carbonates in the acid medium controlled the rate and extent of Cd and Zn sorption. The authors concluded that Cd and Zn were retained by an exchange mechanism only after the pH of the system reached equilibrium (pH 5.5), allowing time for significant transport of these metals. Copper sorption was independent of calcite dissolution. The soil with the higher carbonate content (30%) showed a significant drop in pH (pH 9.1 to 6.6) with the addition of the acid leachate but had sufficient carbonates to buffer the system and sorbed all three metals.

Kotuby-Amacher and Gambrell (1988) studied the retention of Cd and Pb on subsurface soils using a synthetic municipal waste leachate and a synthetic acid metal waste leachate, compared with $Ca(NO_3)_2$ as the background solution. Sorption of the two metals was diminished in the presence of both synthetic leachates. The presence of competing cations and complexing organic and inorganic ligands in the synthetic wastes decreased the retention of Cd and Pb by the soils. Boyle and Fuller (1987) used soil columns packed with five different soils to evaluate the mobility of Zn in the presence of simulated municipal solid waste leachate with various amounts of total organic carbon (TOC) and total soluble salts (TSS). Zinc transport was enhanced in the presence of higher TOC and TSS. Soil properties considered important for retaining Zn in this study were surface area, CEC, and percent clay content. The authors, however, concluded that the leachate composition was more important than soil properties for determining the mobility of Zn.

Puls et al. (1991) studied the sorption of Pb and Cd on kaolinite in the presence of three organic acids, 2,4-dinitrophenol, p-hydroxybenzoic acid, and o-toluic acid. The acids were selected based on their frequent occurance at hazardous waste sites and their persistence in soils. Sorption of Pb decreased in the presence of all the acids due to the formation of 1:2 metal-organic complex resulting in an

uncharged form of Pb. Sorption of Cd decreased in the presence of two of the acids but increased in the presence of 2,4-dinitrophenol. The authors attributed the increase in sorption as being due to either direct sorption of the acid to the clay with the subsequent sorption of Cd or to the enhanced sorption of the 1:1 complex formed between Cd and the acid.

Sheets and Fuller (1986) studied the transport of Cd through soil columns with 0 to 100% ethylene glycol or 2-propanol as the leaching solution. Soils sorbed less Cd from the ethylene glycol solutions than when the columns were leached with water. The 2-propanol increased sorption in one of the soils tested. The effect on Cd sorption was attributed to the change in soil permeability and surface characterization due to the presence of the solvents.

Metal mobility in soil-waste systems is determined by the type and quantity of soil surfaces present, the concentration of metal of interest, the concentration and type of competing ions and complexing ligands, both organic and inorganic, pH, and redox status. Generalization can only serve as rough guides of the expected behavior of metals in such systems. Use of literature or laboratory data that do not mimic the specific site soil and waste system will not be adequate to describe or predict the behavior of the metal. Data must be site specific. Long term effects also must be considered. As organic constituents of the waste matrix degrade, or as pH or redox conditions change, either through natural processes of weathering or human manipulation, the potential mobility of the metal will change as soil conditions change. Few long term studies have been reported.

Behavior of Specific Metals

Copper

Copper is retained in soils through exchange and specific adsorption mechanisms. At concentrations typically found in native soils, Cu precipitates are unstable. This may not be the case in waste-soil systems and precipitation may be an important mechanism of retention. Cavallaro and McBride (1978) suggested that a clay mineral exchange phase may serve as a sink for Cu in noncalcareous soils. In calcareous soils, specific adsorption of Cu onto $CaCO_3$ surfaces may control Cu concentration in solution (Cavallaro and McBride, 1978; Dudley, et al., 1988; Dudley et al., 1991; McBride and Bouldin, 1984). As reported in the adsorption sequence in Table 2, Cu is adsorbed to a greater extent by soils and soil constituents than the other metals studied, with the exception of Pb. Copper, however, has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase Cu mobility in soils.

Zinc

Zinc is readily adsorbed by clay minerals, carbonates, or hydrous oxides. Hickey and Kittrick (1984), Kuo et al. (1983), and Tessier et al. (1980) found that the greatest percent of the total Zn in polluted soils and sediments was associated with Fe and Mn oxides. Precipitation is not a major mechanism of retention of Zn in soils because of the relatively high solubility of Zn compounds. Precipitation may become a more important mechanism of Zn retention in soil-waste systems. As with all cationic metals, Zn adsorption increases with pH.

Zinc hydrolysizes at pH>7.7 and these hydrolyzed species are strongly adsorbed to soil surfaces. Zinc forms complexes with inorganic and organic ligands that will affect its adsorption reactions with the soil surface.

Cadmium

Cadmium may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate. Evidence suggests that adsorption mechanisms may be the primary source of Cd removal from soils (Dudley et al., 1988, 1991). In soils and sediments polluted with metal wastes, the greatest percentage of the total Cd was associated with the exchangeable fraction (Hickey and Kittrick, 1984; Tessier et al., 1980; Kuo et al., 1983). Cadmium concentrations have been shown to be limited by $CdCO_3$ in neutral and alkaline soils (Santillan-Medrano and Jurinak, 1975). As with all cationic metals, the chemistry of Cd in the soil environment is, to a great extent, controlled by pH. Under acidic conditions Cd solubility increases and very little adsorption of Cd by soil colloids, hydrous oxides, and organic matter takes place. At pH values greater than 6, cadmium is adsorbed by the soil solid phase or is precipitated, and the solution concentrations of cadmium are greatly reduced. Cadmium forms soluble complexes with inorganic and organic ligands, in particular Cl-. The formation of these complexes will increase Cd mobility in soils.

Lead

Soluble lead added to the soil reacts with clays, phosphates, sulfates, carbonates, hydroxides, and organic matter such that Pb solubility is greatly reduced. At pH values above 6, lead is either adsorbed on clay surfaces or forms lead carbonate. Of all the trace metals listed in Table 2, Pb is retained by soils and soil constituents to the greatest extent under the conditions of these studies. Most studies with Pb, however, have been performed in well defined, simple matrices, i.e., 0.01M $CaCl_2$. Puls et al. (1991), and Kotuby-Amacher and Gambrell (1988) have demonstrated decrease sorption of Pb in the presence of complexing ligands and competing cations. Lead has a strong affinity for organic ligands and the formation of such complexes may greatly increase the mobility of Pb in soil.

Nickel

Nickel does not form insoluble precipitates in unpolluted soils and retention for Ni is, therefore, exclusively through adsorption mechanisms. Nickel will adsorb to clays, iron and manganese oxides, and organic matter and is thus removed from the soil solution. The formation of complexes of Ni with both inorganic and organic ligands will increase Ni mobility in soils.

Silver

Published data concerning the interaction of silver with soil are rare. As a cation it will participate in adsorption and precipitation reactions. Silver is very strongly adsorbed by clay and organic matter and precipitates of silver, AgCl, Ag_2SO_4 and $AgCO_3$, are highly insoluble (Lindsay, 1979). Silver is highly immobile in the soil environment.

Mercury

The distribution of mercury species in soils, elemental mercury (Hg^o), mercurous ions (Hg_2^{2+}) and mercuric ions (Hg^{2+}), is dependent on soil pH and redox potential. Both the mercurous and mercuric mercury cations are adsorbed by clay minerals, oxides, and organic matter. Adsorption is pH dependent, increasing with increasing pH. Mercurous and mercuric mercury are also immobilized by forming various precipitates. Mercurous mercury precipitates with chloride, phosphate, carbonate, and hydroxide. At concentrations of Hg commonly found in soil, only the phosphate precipitate is stable. In alkaline soils, mercuric mercury will precipitate with carbonate and hydroxide to form a stable solid phase. At lower pH and high chloride concentration, $HgCl_2$ is formed. Divalent mercury also will form complexes with soluble organic matter, chlorides, and hydroxides that may contribute to its mobility (Kinniburgh and Jackson, 1978).

Under mildly reducing conditions, both organically bound mercury and inorganic mercury compounds may be degraded to the elemental form of mercury, Hg^o. Elemental mercury can readily be converted to methyl or ethyl mercury by biotic and abiotic processes (Roger, 1976, 1977). These are the most toxic forms of mercury. Both methyl and ethyl mercury are volatile and soluble in water. Griffin and Shimp (1978) estimated that the removal of Hg from a leachate was not due to adsorption by clays, but was due to volatilization and/or precipitation. This removal of mercury increased with pH. Rogers (1979) also found large amounts of mercury volatilized from soils. Amounts of mercury volatilized appeared to be affected by the solubility of the mercury compounds added to soil. Volatilization was also found to be inversely related to soil adsorption capacity. The form of Hg lost from the soil, whether elemental Hg or methylmercury, was not determined in this study.

Arsenic

In the soil environment arsenic exists as either arsenate, As(V) (AsO_4^{3-}), or as arsenite, As(III) (AsO_2^-). Arsenite is the more toxic form of arsenic.

The behavior of arsenate in soil is analogous to that of phosphate, because of their chemical similarity. Like phosphate, arsenate forms insoluble precipitates with iron, aluminum, and calcium. Iron in soils is most effective in controlling arsenate's mobility. Arsenite compounds are reported to be 4-10 times more soluble than arsenate compounds.

Griffin and Shimp (1978), in a study of arsenate adsorption by kaolinite and montmorillonite, found maximum adsorption of As(V) to occur at pH 5. Adsorption of arsenate by aluminum and iron oxides has shown an adsorption maximum at pH 3-4 followed by a gradual decrease in adsorption with increasing pH (Hingston et al., 1971; Anderson et al., 1976). The mechanism of adsorption has been ascribed to inner sphere complexation (specific adsorption), which is the same mechanism controlling the adsorption of phosphate by oxide surfaces (Hingston et al., 1971; Anderson et al., 1976; Anderson and Malotky, 1979).

The adsorption of arsenite, As(III), is also strongly pH-dependent. Griffin and Shimp (1978) observed an increase in

sorption of As (III) by kaolinite and montmorillonite over a pH range of 3-9. Pierce and Moore (1980) found the maximum adsorption of As(III) by iron oxide occurred at pH 7. Elkhatib et al. (1984b) found adsorption of As(III) to be rapid and irreversible on ten soils. They determined, in this study and another study (Elkhatib et al., 1984a), that Fe oxide, redox, and pH were the most important properties in controlling arsenite adsorption by these soils.

Both pH and the redox are important in assessing the fate of arsenic in soil. At high redox levels, As(V) predominates and arsenic mobility is low. As the pH increases or the redox decreases As (III) predominates. The reduced form of arsenic is more subject to leaching because of its high solubility. The reduction kinetics are, however, slow. Formation of As (III) also may lead to the volatilization of arsine (AsH_3) and methyl-arsines from soils (Woolson 1977a). Under soil conditions of high organic matter, warm temperatures, adequate moisture, and other conditions conducive to microbial activity, the reaction sequence is driven towards methylation and volatil-ization (Woolson 1977a). Woolson's (1977b) study showed that only 1 to 2 percent of the sodium arsenate applied at a rate of 10 ppm was volatilized in 160 days. The loss of organic arsenical compounds from the soil was far greater than for the inorganic source of arsenic. Arsenite, As(III), can be oxidized to As(V). Manganese oxides are the primary electron acceptor in this oxidation (Oscarson et al., 1983).

Selenium

The behavior of selenium in soils has received great attention in recent years. Studies were stimulated by the high incidence of deformity and mortality of waterfowl at the Kesterson National Wildlife Refuge in California that resulted from the input of agricultural drainage water from the western San Joaquin Valley that was high in Se. Such studies have led to a better understanding of the distribution and movement of Se in soils and ground water.

Selenium exists in the soil environment in four oxidation states: selenide (Se^{2-}), elemental selenium (Se^o), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}). The concentration and form of Se in soil is governed by pH, redox, and soil composition. Selenate, Se(VI), is the predominant form of selenium in calcareous soils and selenite, Se(IV), is the predominant form in acid soil.

Selenite, Se (IV) binds to sesquioxides, especially to Fe oxides. Balistriera and Chao (1987) found the removal of selenite by iron oxide to increase with decreasing pH. This study not only demonstrates the effect of pH on selenite adsorption but also the effect of concentration. The decrease in the percentage of selenite adsorbed with increasing concentration of selenite at a given pH indicated multiple sites of selenite retention. At the two lower concentrations, high energy specific adsorption sites were available. As the concentration of selenite was increased these sites became saturated and the lower energy sites were utilized. Griffin and Shimp (1978) found maximum adsorption of selenite on montmorillonite and kaolinite to occur at pH 2-3. Neal et al. (1987a) used five soils from the San Joaquin Valley and found that selenite adsorption by the soils decreased with increasing pH in the range of 4-9. Selenite adsorption to oxides and soils occurs through an inner sphere complexation (specific adsorption) mechanism (Rajan, 1979; Neal et al., 1987b).

In studies of competitive adsorption using phosphate, sulfate, and chloride (Neal, et al., 1987b) and phosphate and various organic acids (Balistrieri and Chao, 1987), selenite adsorption decreased dramatically in the presence of phosphate and the organic acids but was not affected by the presence of sulfate or chloride. Balistrieri and Chao (1987), using Fe oxide, found the sequence of adsorption to be: phosphate = silicate = arsenate > bicarbonate carbonate > citrate = selenite > molybdate > oxalate > fluoride = selenate > sulfate. Precipitation is not a major mechanism of retention of selenite in soils. Manganese selenite may form, however, in strongly acidic environments (Elrashidi et al., 1989).

Selenate dominates under alkaline conditions. In contrast to selenite, selenate, Se(VI), is highly mobile in soils. Benjamin (1983) found that selenate was adsorbed by amorphous iron oxide as a function of pH. Maximum removal was at pH 4.5 and adsorption decreased with increasing pH. Bar-Yosef and Meek (1987) found some indication of selenate adsorption by kaolinite below pH 4. Selenate seems to be adsorbed by weak exchange mechanisms similar to sulfate (Neal and Sposito, 1989), in contrast to selenite that is specifically adsorbed by soils and soil constituents. There has been some evidence that selenate was adsorbed by alkaline soils (Singh et al., 1981), but Goldberg and Glaubig (1988) found no removal of selenate by calcareous montmorillonite. Neal and Sposito (1989), using soils from the San Joaquin Valley, showed no adsorption of added selenate over a pH range from 5.5-9.0. Fio et al. (1991) also observed no sorption of selenate by alkaline soil from the San Joaquin Valley, but did observe the rapid sorption of selenite by this soil. No stable precipitates of selenate are expected to form under the pH and redox conditions of most soils (Elrashidi, et al., 1989).

Similar to other anionic species, selenium is more mobile at higher pHs. Soil factors favoring selenium mobility, as summarized by Balistrieri and Chao (1987) are; alkaline pH, high selenium concentration, oxidizing conditions, and high concentrations of additional anions that strongly adsorb to soils, in particular phosphate.

Under reduced conditions, selenium is converted to the elemental form. This conversion can provide an effective mechanism for attenuation since mobile selenate occurs only under well aerated, alkaline conditions.

Organic forms of selenium are analogous to those of sulfur, including seleno amino acids and their derivatives. Like sulfur, selenium undergoes biomethlyation forming volatile methyl selenides.

Chromium

Chromium exists in two possible oxidation states in soils: the trivalent chromium, Cr(III) and the hexavalent chromium, Cr(VI). Forms of Cr(VI) in soils are as chromate ion, $HCrO_4^-$ predominant at pH<6.5, or CrO_4^{2-}, predominant at pH 6.5, and as dichromate, $Cr_2O_7^{2-}$ predominant at higher concentrations (>10mM) and at pH 2-6. The dichromate ions pose a greater health hazard than chromate ions. Both Cr(VI) ions are more toxic than Cr(III) ions. Reviews of the processes that control the fate of chromium in soil and the effect these processes have on remediation are given in Bartlett (1991) and Palmer and Wittbrodt (1991).

Because of the anionic nature of Cr(VI), its association with soil surfaces is limited to positively charged exchange sites, the number of which decreases with increasing soil pH. Iron and aluminum oxide surfaces will adsorb CrO_4^{2-} at acidic and neutral pH (Davis and Leckie, 1980; Zachara et al., 1987; Ainsworth et al., 1989). Stollenwerk and Grove (1985) concluded that the adsorption of Cr(VI) by ground-water alluvium was due to the iron oxides and hydroxides coating the alluvial particles. The adsorbed Cr(VI) was, however, easily desorbed with the input of uncontaminated ground water, indicating nonspecific adsorption of Cr(VI). The presence of chloride and nitrate had little effect on Cr(VI) adsorption, whereas sulfate and phosphate inhibited adsorption (Stollenwerk and Grove, 1985). Zachara et al. (1987) and Zachara et al. (1989) found SO_4^{2-} and dissolved inorganic carbon inhibited Cr(VI) adsorption by amorphous iron oxyhydroxide and subsurface soils. The presence of sulfate, however, enhanced Cr(VI) adsorption to kaolinite (Zachara et al., 1988). Rai et al. (1988) suggested that BaCrO4 may form in soils at chromium contaminated waste sites. No other precipitates of hexavalent compounds of chromium have been observed in a pH range of 1.0 to 9.0 (Griffin and Shimp, 1978). Hexavalent chromium is highly mobile in soils.

In a study of the relative mobilities of 11 different trace metals for a wide range of soils, Korte et al. (1976) found that clay soil, containing free iron and manganese oxides, significantly retarded Cr(VI) migration (see Figure 6). Hexavalent chromium was found to be the only metal studied that was highly mobile in alkaline soils. The parameters that correlated with Cr(VI) immobilization in the soils were free iron oxides, total manganese, and soil pH, whereas the soil properties, cation exchange capacity, surface area, and percent clay had no significant influence on Cr(VI) mobility.

Rai et al. (1987) reported that Cr(III) forms hydroxy complexes in natural water, including $Cr(OH)_2^+$, $Cr(OH)^{2+}$, $Cr(OH)_3^o$, and $Cr(OH)_4^-$. Trivalent chromium is readily adsorbed by soils. In a study of the relative mobility of metals in soils at pH 5, Cr(III) was found to be the least mobile (Griffin and Shimp, 1978). Hydroxy species of Cr(III) precipitate at pH 4.5 and complete precipitation of the hydroxy species occurs at pH 5.5.

Hexavalent chromium can be reduced to Cr(III) under normal soil pH and redox conditions. Soil organic matter has been identified as the electron donor in this reaction (Bartlett and Kimble, 1976; Bloomfield and Pruden, 1980). The reduction reaction in the presence of organic matter proceeds at a slow rate at environmental pH and temperatures (Bartlett and Kimble, 1976; James and Bartlett, 1983a,b,c). Bartlett (1991) reported that in natural soils the reduction reaction may be extremely slow, requiring years. The rate of this reduction reaction, however, increases with decreasing soil pH (Cary et al., 1977; Bloomfield and Pruden, 1980). Soil organic matter is probably the principal reducing agent in surface soils. In subsurface soils, where organic matter occurs in low concentration, Fe(II) containing minerals reduce Cr(VI) (Eary and Rai, 1991). Eary and Rai (1991), however, observed that this reaction only occurred in the subsurface soil with a pH<5. The reduction of Cr(VI) occurred in all four subsurface soils tested by decreasing the pH to 2.5.

Bartlett and James (1979), however, demonstrated that under conditions prevalent in some soils, Cr(III) can be oxidized.

The presence of oxidized Mn, which serves as an electron acceptor, was determined as an important factor in this reaction.

Industrial use of chromium also includes organic complexed Cr(III). Chromium (III) complexed with soluble organic ligands will remain in the soil solution (James and Bartlett, 1983a). In addition to decreased Cr(III) adsorption, added organic matter also may facilitate oxidation of Cr(III) to Cr(VI).

Computer Models

Several equilibrium thermodynamic computer programs are available for modeling soil solution and solid phase chemistry by proving information on the thermodynamic possibility of certain reaction to occur. In addition to calculating the equilibrium speciation of chemical elements in the soil solution and precipitate/dissolution reactions, models such as GEOCHEM (Mattigod and Sposito, 1979) and MINTEQA2 (USEPA, 1987) provide information on cation exchange reactions and metal ion adsorption. These models are used to:

1) calculate the distribution of free metal ions and metal-ligand complexes in a soils solution,

2) predict the fate of metals added to soil by providing a listing of which precipitation and adsorption reactions are likely to be controlling the solution concentration of metals, and

3) provide a method for evaluating the effect that changing one or more soil solution parameters, such as pH, redox, inorganic and organic ligand concentration, or metal concentration, has on the adsorption/precipitation behavior of the metal of interest.

These models are equilibrium models and as such do not consider the kinetics of the reactions. These models are also limited by the accuracy of the thermodynamic data base available.

Analysis of Soil Samples

Total concentration of metals in soil

Measurement of the total concentration of metals in soils is useful for determining the vertical and horizontal extent of contamination and for measuring any net change (leaching to ground water, surface runoff, erosion) in soil metal concentration over time. The methods do not, however, give an indication as to the chemical form of the metal in the soil system.

The complete dissolution of all solid phase components in soils requires a rigorous digestion using either a heated mixture of nitric acid, sulfuric acid, hydrofluoric acid, and perchloric acid (Page et al., 1982) or a fusion of the soil with sodium carbonate (Page et al., 1982). Both methods require special equipment and special safety considerations. A more commonly used procedure is the hot nitric acid-hydrogen peroxide procedure outlined in SW-846 Method 3050 (USEPA, 1986). This is a partial digestion of the soil solid phase. The method probably releases metals associated

with a recent pollution source, i.e., exchangeable, specifically adsorbed to clays, oxides or organic matter, and most precipitates, but would not release metals associated within solid phases that are not dissolved by the hot nitric acid and oxidizing agent, i.e., within the structure of insoluble minerals.

Sequential extractions of metals in soils

Since the potential migration of metals in soil systems is dependent on the chemical form of the metal, extraction procedures have been developed to selectively remove metals from these various geochemical forms. While these procedures cannot be used to identify the actual form of a given metal in a soil, they are useful in categorizing the metals into several operationally defined geochemical fractions, such as exchangeable, specifically adsorbed, and metals associated with carbonates, organic matter, and/or iron and manganese oxides.

Numerous extraction procedures have been developed for metal cations (Sposito et al., 1984; Hickey and Kittrick, 1984; Tessier et al., 1979; Grove and Ellis, 1980; Kuo et al., 1983) and anions (Chao and Sanzolone, 1989; Gruebel et al., 1988). Lake et al. (1984) reviewed a number of the procedures used for cationic metal extraction. The extraction procedures consist of reacting a soil sample with increasing strengths of chemical solutions. Typically water or a salt solution (KNO_3, $CaCl_2$, etc.) is the first extractant used. These are followed by mild acids, bases, chelating agents, and oxidizing solutions. Table 4 illustrates the wide variety of extractants that have been used in the literature for metal cations.

The aqueous fraction and those fractions in equilibrium, i.e., the exchange fraction, with this fraction are of primary importance when considering the migration potential of metals in soils. In theory, mild extractants, such as salt solutions, are more likely to extract metals that could be released to the soil solution with input of water than metals associated with stronger binding mechanisms, such as specifically adsorbed or precipitated metals. Work by Silveira and Sommers (1977) and Latterell et al. (1978) suggests that salt extractable metals represent the potentially mobile portion of the total concentration of metals in soils. Harrison et al. (1981) likewise suggested that the mobility of metals decreases in the order of the extraction sequence. Rigorous evaluation, however, of the appropriateness of any extraction procedure for defining the mobile fraction of metals in soils has not been reported in the literature.

Hickey and Kittrick (1984) used a sequential extraction procedure to separate Cd, Cu, Ni, and Zn in metal polluted soils and sediments into five operationally defined geochemical fractions: exchangeable (1.0M $MgCl_2$), metals associated with carbonates (acetate buffer, pH 5), metals associated with Mn and Fe oxides (0.04M $NH_4OH \cdot HCl$), metals associated with organic matter (0.02M $HNO_3 + H_2O_2$), and residual metals (HF+$HClO_4$). Figure 10 shows the average distribution of the metals among the defined geochemical fractions. Approximately 37% of the total Cd and a significant portion of the Zn were in the exchange fraction indicating the potential mobility of these two metals. Only a small portion of the Cu and Ni were in the exchange fraction. A significant portion of the Cu was associated with the organic fraction, in agreement with the known affinity of Cu for organic material. Nickel was mostly associated with the residual
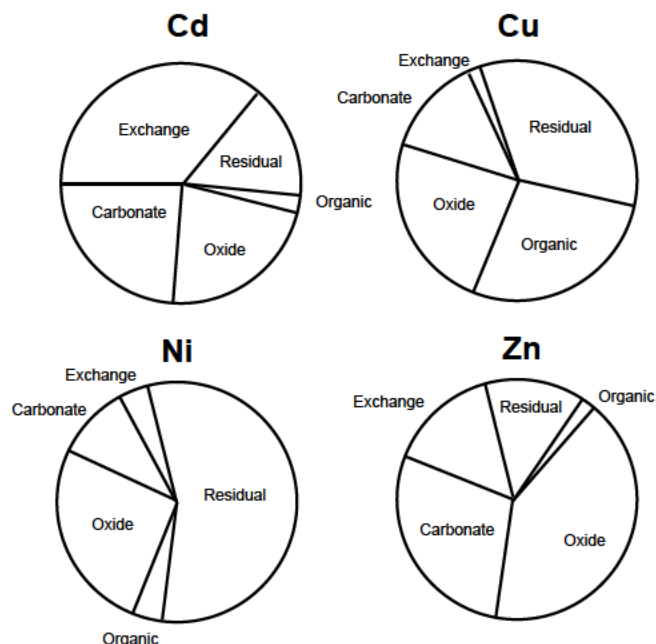
Figure 10. Proportions of Cd, Cu, Ni, and Zn in each of the operationally defined geochemical fractions of the experimental samples (Hickey and Kittrick, 1984).

fraction and significant portions of Zn and Cu were associated with the oxides. The authors concluded from this study that the relative mobility of the metals followed: Cd > Zn > Cu = Ni.

There has been recent criticism of these sequential extraction procedures (Miller et al., 1986; Kheboian and Bauer, 1987; Gruebel et al., 1988; Tipping et al., 1985; Rapin et al., 1986; Calvet et al., 1990). The methods are not entirely specific for a geochemical fraction of the soil and the extractant also may remove metals associated with other fractions. Secondly, readsorption of the extracted metals to the remaining solid phase of the soil may occur leading to artificially low concentrations of the metal being associated with that fraction. Finally, no one extraction procedure would be universally applicable for all metals and all soils. Perhaps the most suitable extractant for defining the mobile fraction of metals in soils under specific site conditions is one that simulates that soil or soil-waste solution chemistry.

TCLP

The Toxicity Characterization Leaching Procedure (TCLP) (USEPA, 1986) is a single extraction procedure, using 0.1M acetic acid, developed to simulate the leaching a waste might undergo if disposed of in a municipal landfill. This method is frequently used to determine the leaching potential of cationic metals in landfill situations where, due to microbial degradation of the waste under anaerobic conditions, acetic acid is produced. While this procedure is appropriate for demonstrating whether an excavated metal contaminated soil is defined as hazardous for disposal at a landfill, its application

Table 4. Some bibliographic data on the extraction of heavy metals present in soils and sediments (Colvet, et al., 1990)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and residual fraction
McLaren Crawford[11] (1973)	0.05 N $CaCl_2$	2.5% CH_3COOH	0.1 M $(COOH)_2$ +0.175 M $(COONH_4)_2$ pH = 3.5	1 M $K_4P_2O_7$	HF
Stover et al.[12] (1976)	1 M KNO_3 +NaF		0.1 M EDTA pH = 6.5	0.1 M $Na_4P_2O_7$	1 M HNO_3
Gatehouse et al.[13] (1977)		1 M CH_3COONH_4 +CH_3COOH pH = 4.5	0.1 M NH_2OH +1 M CH_3COONH_4 pH = 4.5	30% H_2O_2	$HF-HClO_4$
Filipek and Owen[14] (1979)		1 M CH_3COOH	0.25 M NH_2OH, HCl in 25% (v/v) CH_3COOH	Acidified 30% H_2O_2	$HNO_3-HF-HClO_4$
Tessier et al.[3] (1979)	1 M $MgCl_2$ or 1 M CH_3COONa at pH = 8.2	1 M CH_3COONa + 1 M CH_3COOH at pH = 5.0	0.04 M NH_2OH, HCl in 25% (v/v) CH_3COOH at 96 ± 3°C or 0.3 M $Na_2S_2O_4$ +0.175 M Na—citrate +0.025 M citric acid	0.02 M HNO_3+ 30% H_2O_2, pH = 2 at 85 ± 2°C, 2 h +30% H_2O_2+HNO_3, pH = 2 at 85 ± 2°C, 3 h 3.2 M CH_3COONH_4 in 20% HNO_3	$HF-HClO_4$
Förstner et al.[2] (1979)	0.2 M $BaCl_2$		0.1 M NH_2OH, HNO_3 + 25% (v/v) CH_3COOH + HCl	30% H_2O_2 + NH_4OH	$HF-HClO_4$
Schalscha et al.[4] (1980)	1 M KNO_3	0.5 M NaF pH = 6.5	0.1 M EDTA pH = 6.5 double extraction	0.1 M $Na_4P_2O_5$	1 M HNO_3
Garcia-Miragaya[15] (1981)	1 N $CaCl_2$	2.5% CH_3COOH	0.05 M EDTA pH = 7	0.1 N $Na_4P_2O_5$	HF
Badri and Aston[16] (1981)		1 M CH_3COONH_4 +0.5 M $(CH_3COO)_2$ Mg	0.25 M NH_2OH, HCl pH = 2	30% H_2O_2 + 1 M CH_3COONH_4	
Förstner et al.[17] (1981)	1 M CH_3COONH_4 pH = 7		(1) 0.1 M NH_2OH, ClH +0.0I M HNO_3, pH = 2 (2) 0.2 M $(COONH_4)2$ +0.2 M $(COOH)2$, pH = 3	30% H_2O_2, HNO_3 pH = 2 at 85°C extraction with 1 M CH_3COONH_4	HNO_3 at 180°C
Greffard et al.[6] (1981)		resin-H^+	(1) $(COONa)_2$ (2) $(COONa)_2$ + UV	30% H_2O_2 at 40°C	
Sposito et al.[10]	0.5 M KNO_3		0.5 M Na_2 EDTA	0.5 M NaOH	4 M HNO_3 at 80°C
Dekeyser et al.[18] (1983)		1M CH_3COONH_4 pH = 4.5	(1) 0.1 M NH_2OH, HCl (2) 0.2 M $(COONH_4)_2$ $(HCOOH)2$, pH = 3.3 obscurité (3) Same as (2)+UV		$HNO_3-HF-HCl$
Kuo et al.[7] (1983)	1 M $MgCl_2$		(1) $(COONa)2$ (2) Citrate dithionite bicarbonate	6% $NaClO_4$ at 85°C	HNO_3-HClO_4
Meguelatti et al.[5] (1983)	1 M $BaCl_2$	1 M CH_3COOH +0.6 M CH_3COONa	0.1 M NH_2OH +25% (v/v) CH_3COOH	30% H_2O_2 +0.02 M HNO_3 +3.2 M CH_3COONH_4	HF-HCl
Shuman[19] (1985)	1 M $Mg(NO_3)_2$ pH = 7		(1) 0.1 M NH_2OH, HCl pH = 2 (2) 0.2 M $(COONH_4)2$ +0.2 M $(COOH)2$, pH = 3 (3) Same as (2) + ascorbic acid	0.7 M NaOCl pH = 8.5	$HF-HNO_3-HCl$
Gibson and Farmer[20] (1986)	1 M CH_3COONH_4 pH = 7	1 M CH_3COONa pH = 5	(1) 0.1 M NH_2OH, ClH +0.01 M HNO_3 (2) 1 M NH_2OH, ClH in 25% (v/v) CH_3COOH	30% H_2O_2 +0.02 M HNO_3 at 85 °C	Aqua regia + HF

for evaluating the mobility of metals under field conditions has been questioned (Dragun et al., 1990). Production of acetic acid does not commonly occur in soils. In certain soil-waste systems, leaching tests using acetic acid may be appropriate, but it is not universally representative of the leaching solution for soil-waste systems. The acetic acid leaching procedure was developed for cationic metals. The procedure is not appropriate for extraction of anionic metals. Bartlett (1991) reported that this procedure actually causes the reduction of Cr(VI) to Cr(III) leading to a false measurement of the leachability of Cr(VI) in soil. A more appropriate leaching solution would mimic the specific waste or waste-soil matrix.

Hickey and Kittrick (1984) used an acetate buffer solution in their sequential extraction scheme to remove metals associated with carbonates. This is a similar solution to the TCLP solution except that it is buffered to pH 5. This buffered solution fully dissolves the carbonate minerals in the soil. The unbuffered acetic acid solution used in the TCLP solution cannot maintain a low enough pH in calcareous soils to dissolve carbonates. The metals extracted by the TCLP solution are not related to any definable geochemical fraction and the fraction of metals extracted using this procedure have not been correlated with the mobile fraction of metals in soil.

Evaluating the Behavior of Metals in Soils

Sorption studies

Soil sorption studies are commonly performed to evaluate the extent of metal retention by a soil or soil constituent. Sorption studies are often used in an attempt to generate the equilibrium distribution coefficient (Kd), the ratio of metal sorbed to metal in solution at equilibrium, which may be utilized in transport models. Sorption studies are also used for comparison of the relative retention of several metals by a soil or the relative retention of a metal by several soils, and are used extensively in correlation studies to determine the relative importance of a soil's chemical and physical properties for metal retention. Sorption studies also can be used to evaluate the effect that changing a soil solution parameter, e.g., adjustment of pH, ionic strength, addition of competing cations, or addition of inorganic or organic ligands, has on metal retention by a soil.

In a sorption study, the soil is reacted with solutions containing varying quantities of the metal(s) of interest for a specified time period using either batch or column techniques. The concentration range used in the study should overlap the concentration of environmental concern. A background electrolyte solution also should be used to simulate normal soil's solution chemistry or the waste matrix and to equalize the ionic strength across all soils. The reaction time should approach thermodynamic equilibrium, usually determined by a preliminary kinetics experiment. After the specified time period the soil and solution are separated by centrifugation and/or filtration. The soil and/or solution phases are then analyzed by atomic absorption spectrophotometry or inductively coupled plasma emission spectrometry. With these techniques it is not possible to distinguish between true adsorption and precipitation reactions. For that reason the term sorption will be used.

Two techniques, batch and column studies, may be used to generate sorption isotherms. The batch technique involves placing the soil and the solutions containing the various concentrations of the metals into a vessel and mixing the samples for a prescribed time period. This is the most commonly used technique because of its ease of laboratory operation and ease of data handling. The disadvantages of the technique are 1) results are sensitive to the soil:solution ratio used, 2) soil:solution ratios in actual soil systems cannot be done in batch studies, so scaling of data from batch studies to soils systems is uncertain, 3) results are sensitive to the mixing rate used, 4) separation techniques may affect results, and 5) many investigators have found that batch generated sorption coefficients are not adequate to describe the behavior of metals in flow through systems.

The column method consists of packing a glass or plastic column with soil. The solutions containing various concentrations of the metals of interest are pumped through the columns and the effluents are collected and analyzed by AA or ICP. Breakthrough occurs when the effluent concentration equals the influent concentration. The advantages of this technique are 1) low soil:solution ratios can be used, 2) separation of the soil and solution phase is not required, 3) mechanical mixing is not required and 4) column studies more closely simulate field conditions than batch methods. The disadvantages are 1) results depend on flow rates used, 2) columns are difficult to set-up and maintain, 3) uniform packing of the column is difficult often leading to channel flow, and 4) fewer columns can be operated at one time compared with the number of batch reactors.

Equilibrium sorption is described by a sorption isotherm. A sorption isotherm is the relationship between the amount of metal sorbed and the equilibrium concentration of the metal or, more correctly, the activity of the free metal in the soil solution. A typical sorption isotherm is shown in Figure 11. If the relationship is linear over the concentration range studied then the sorption process can be described by a single coefficient, the distribution coefficient, Kd. For metals, however, the relationship is seldom linear and other equations with two or more coefficients must be used to describe the data.
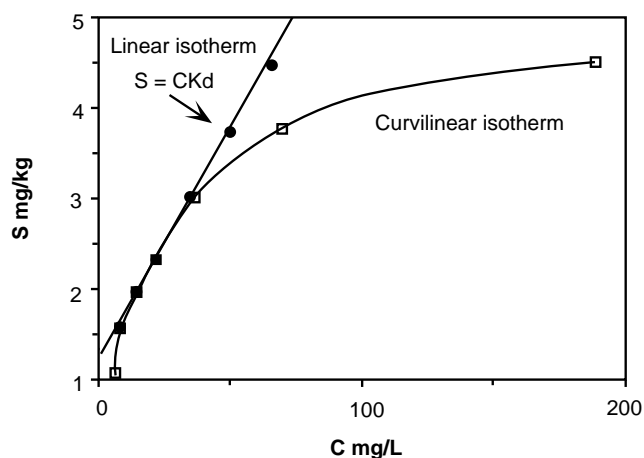
Figure 11. Sorption isotherms.

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Equations most frequently used, because of their relative simplicity, to describe the curvilinear sorption behavior of metals in soil are the Langmuir and the Freundlich equations. The Langmuir equation was developed to model gas adsorption on solid surfaces. The derivation of the equation was based on the assumption that adsorption is independent of surface coverage, that there is no interaction between adsorbed ions, and that only a monolayer of adsorption occurs on the surface. These conditions are not typically met with metals sorption on soils.

The linearized form of the Langmuir equation is:

$$\frac{C}{S} = \frac{C}{M} + \frac{1}{Mb} \qquad (1)$$

where C is the concentration or activity of the free metal in solution, S is the quantity of the metal ion sorbed by the soil (i.e., mg metal sorbed/Kg soil), M is the maximum sorption capacity of the soil, and b is the coefficient related to bonding energy. When C/S is plotted as a function of C, the slope is the reciprocal of the sorption capacity, M, and the intercept is 1/Mb.

The Freundlich expression is an empirically derived equation to describe the logarithmic decrease in adsorption energy with increasing surface coverage. The linearized form of the Freundlich equation is:

$$\log S = (N)\log C + \log K \qquad (2)$$

where S and C have the same definition as above and N and K are constants fitted from the experimental data. When the slope, N, equals 1, the equation simplifies to:

$$S = CK_d \text{ or } K_d = S/C \qquad (3)$$

where K_d is the distribution coefficient. In most studies reported in the literature for metal sorption, the slope of the Freundlich isotherm is seldom equal to 1 and the simplified expression and its single term, K_d, are not appropriate to describe the data.

Figure 12 illustrates the use of the Langmuir expression to describe Cu sorption by a soil (Cavallaro and McBride, 1978). The equation describes the behavior of Cu over all concentrations used in this study. Often, however, nonlinear behavior over the concentration range studied is observed with the use of either the Langmuir or Freundlich equations. In Figure 13, the Langmuir expression was used to describe the sorption behavior of Cd and Zn by hydrous manganese oxide (Zasoski and Burau, 1988). This non-linear behavior when using the Langmuir equation has been noted by numerous researchers using various metals and soils and soil constituents (Benjamin and Leckie, 1981; Shuman, 1975; Loganathan and Burau, 1973). Non-linearity of metal sorption using the Freundlich equation has also been noted by Zasoski and Burau (1988) Benjamin and Leckie (1981), Catts and Langmuir (1986), O'Connor et al. (1984), O'Connor et al. (1983), and Elrashdi and O'Connor (1982). This non-linear behavior has been interpreted to indicate multiple sites of sorption that have different energies of retention. The mechanisms at low concentrations have been attributed to specific adsorption, whereas the mechanisms at higher concentrations have been considered to be exchange
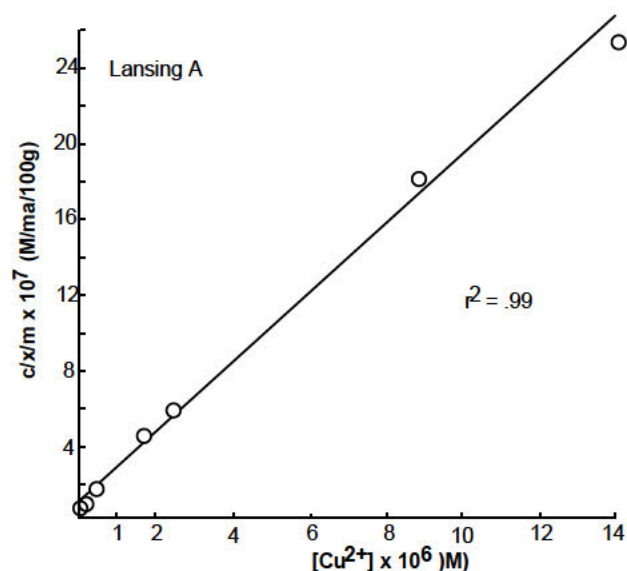
Figure 12. Langmuir adsorption isotherm for Cu^{2+} adsorption on the Lansing A soil (Cavallaro and McBride 1978).
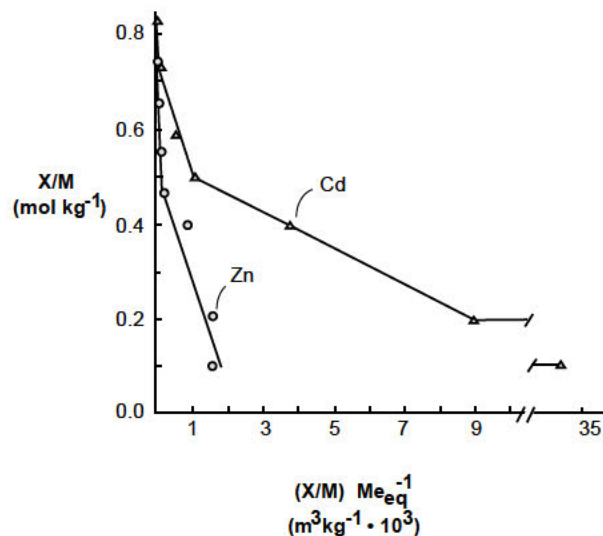
Figure 13. Langmuir plots of Cd and Zn sorbed on δ- MnO_2 for the noncompetitive pH 4 data (Zasoski and Burau, 1988).

reactions or precipitation. These results illustrate the importance of generating sorption data over the concentration range of interest for a particular application. Large error in predicting sorptive behavior may result from using data generated in one system and applied to a system with higher or lower metal concentration.

Several researchers have, however, suggested that other equations, for example the two-surface Langmuir equation (Sposito, 1982; Travis and Etnier, 1981) or the competitive Langmuir equation (Griffin and Au, 1977; Travis and Etnier,

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1981), be used to describe the non-linear behavior encountered with the Langmuir equation (Sposito, 1982).

The Langmuir and Freundlich isotherm expressions have proven valuable in interpreting metal behavior in soils. The adsorption isotherm equations were, however, developed for modeling gas adsorption on solids. The sorption of metals by soils violates many of the assumptions associated with these equations. Also, the mechanism described by these equations is adsorption, but it is impossible in a soil system to distinguish between adsorption and precipitation reactions. Adsorption isotherm equations should not be used to indicate adsorption mechanisms without collaborative evidence, but they can be used for an empirical description of the data. Harter (1984) warned against over interpreting the sorption maximum and "bonding energy" determined using the Langmuir equation. The applicability of adsorption isotherm equations to the interpretation of soil chemical phenomena is a subject of controversy. For further discussion of this controversy see Elprince and Sposito (1981), Griffin and Au (1977), Veith and Sposito (1977), Sposito (1979), Harter and Baker (1977), and Harter (1984).

Desorption

Desorption studies are often performed to determine the reversibility of the sorption reactions. This gives an idea of the strength of the association of the metal with the soil surface. An example of the reversibility of a sorption reaction (Figure 14) is taken from Dudley et al. (1988). In this study, two calcareous soils were reacted with various concentrations of Cd. The soils were then desorbed with $CaCl_2$. For the low carbonate soil (Kidman) virtually all of the sorbed Cd was desorbed by the Ca. Only 10-15 percent of the sorbed Cd on the highly calcareous Skumpah soil was desorbed by Ca. These results suggest that Cd was held by the Kidman soil as an exchangeable cation, whereas in the Skumpah, Cd was specifically adsorbed by the $CaCO_3$.

Desorption studies are performed after completion of the sorption study. They can be carried out using either batch or column techniques. For the batch technique the soils used in the sorption are reacted with a salt solution, typically 0.01N $CaCl_2$ or a matrix representative of the soil-waste system being studied. Samples are shaken for a specified time period. The soil and liquid are then separated by centrifugation and/or filtration and the solution is analyzed for the metals by AA or ICP. This process is repeated several times. For a column study, the metal equilibrated soil column is flushed with an appropriate solution until the system reaches steady state conditions.

Kinetics

Attention has been mainly given in the literature to equilibrium processes in soils but soil processes are never at equilibrium. Soil systems are dynamic and are thus constantly changing. Most kinetic studies have been performed to establish the proper time interval for use in equilibrium sorption/desorption studies. Most studies assume that ion exchange processes are rapid in soils and that 16 to 24 hours mixing periods, common time periods used in sorption studies, are adequate. This assumption may not be appropriate if other reactions in addition to simple ion exchange, i.e., specific adsorption and precipitation, are involved in metals retention (Harter and Lehmann, 1983). McBride (1980) found that the initial adsorption of Cd on calcite was very rapid, while $CdCO_3$ precipitation of higher Cd^{2+} concentrations was slow. Lehmann and Harter (1984) used kinetics of desorption to study the strength of Cu bonding to a soil. A plot of concentration of Cu in solution versus time indicates an initial rapid release of the Cu followed by a slow reaction. They interpreted these results to indicate that Cu was held at two sites: the rapidly released Cu being loosely held on the soil surfaces and the slowly released Cu being tightly bound.

Each metal-soil system should be tested to determine the time necessary for the individual system to come to equilibrium. Figure 15 illustrates the different time periods required for equilibrium for three metals sorbed by a calcareous soil (Dudley, et al., 1988). Copper reached equilibrium within a few hours whereas Cd and Zn did not approach steady state conditions for 144 hours. Use of the time interval appropriate for Cu equilibrium for this soil would mean that only 50 percent of the Cd and Zn adsorbed under steady state conditions would have been determined.

Kinetic studies are being more widely performed because of their importance in determining the transport of metals in soil systems. Many mathematical transport models now allow a kinetic term for sorption. Equilibrium studies predict whether a reaction will occur but give no indication of the time necessary for the reaction to take place. Kinetic studies also contribute to an understanding of reaction mechanisms not discernible from thermodynamic studies (Zasoski and Burau, 1988; Harter and Smith, 1981; Sparks, 1989).

Kinetic studies are similar to sorption procedures, using either batch or column techniques, except samples are collected over time. Several equations have been used to describe the kinetics of sorption reactions of ions on soils and soil constituents. These equations include: first-order, second-order, Elovich equation, parabolic diffusion equation, and power function equation. An excellent review of kinetic processes in soil systems is given by Sparks (1989).
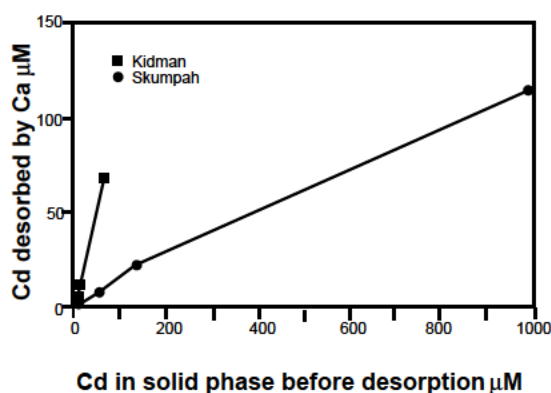
Figure 14. Desorption of Cd from Kidman and Skumpah soil by 0.01 *M* CaCl₂ at a soil:solution ratio of 1:25 (Dudley, et al., 1988).
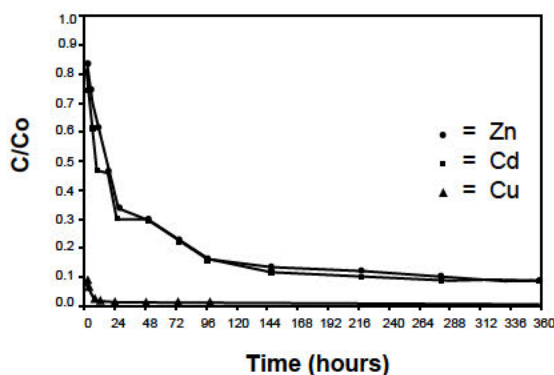
Figure 15. Change with time in reduced concentration of metals in suspensions of the Skumpah soils. C_o was the concentration of metal ions at time = 0 (Dudley, et al., 1988).

Summary

Metals added to soil will normally be retained at the soil surface. Movement of metals into other environmental compartments, i.e., ground water, surface water, or the atmosphere, should be minimal as long as the retention capacity of the soil is not exceeded. The extent of movement of a metal in the soil system is intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix.

The retention mechanisms for metals added to soil include adsorption of the metal by the soil solid surfaces and precipitation. The retention of cationic metals by soil has been correlated with such soil properties as pH, redox potential, surface area, cation exchange capacity, organic mater content, clay content, iron and manganese oxide content, and carbonate content. Anion retention has been correlated with pH, iron and manganese oxide content, and redox potential. In addition to soil properties, consideration must be given to the type of metal and its concentration and to the presence of competing ions, complexing ligands, and the pH and redox potential of the soil-waste matrix. Transport of metals associate with various wastes may be enhanced due to (Puls et al., 1991):

1. facilitated transport caused by metal association with mobile colloidal size particles,
2. formation of metal organic and inorganic complexes that do not sorb to soil solid surfaces,
3. competition with other constituents of waste, both organic and inorganic, for sorption sites, and
4. deceased availability of surface sites caused by the presence of a complex waste matrix.

Because of the wide range of soil characteristics and various forms by which metals can be added to soil, evaluating the extent of metal retention by a soil is site/soil/waste specific. Changes in the soil environment over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix.

Laboratory methods for evaluating the behavior of metals in soils are available in the literature. Thermodynamic equilibrium computer models are also available to assist with this evaluation. The advantages and disadvantages of some of the available procedures have been presented in this document.

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Selenium Location and Mode of Occurrence in the Kanawha Formation Rocks in West Virginia

WEST VIRGINIA MINE DRAINAGE TASK FORCE SYMPOSIUM
April 18-19, 2006

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Hydrogeology Research Center of the WV Water Research Institute

Outline

- Objectives & Purpose

- Project summary

- Total Se distribution

- Se mode of occurrence

- Next steps

Project Objectives

1. How do Se concentrations change in a single core?
   - Stratigraphy (depth), rock type, other chemical parameters

2. How is Se chemically bound to the rocks? (mode of occurrence)
   - Rock type

Purpose

- Better understand the chemistry of selenium in coals and related strata

- Help predict where selenium is most likely to be encountered

Samples Used

1 core from south-central WV

63 samples

- 11 Coal, 25 shale, 9 mudstone, 12 sandstone, 6 carbolith
- Kanawha Formation (Coalburg – Winifrede coal beds)

Sample prep by Research Environmental & Industrial Consultants (REIC)

- Lithology described
- Ground to <60 mesh by lithology
  - <0.5 feet: completely composited
  - >0.5 – 5 feet: ~1-inch interval from top, middle, & bottom of each 1-foot length. Ground to 1/16 inch, composited, then 500 g ground to <60 mesh

Stratigraphic Nomenclature

Coal Beds

Selenium (Se)
Parts-per-million (ppm) on a whole coal basis

							Coal Beds	Se (ppm)	# samples

European Stages — **North American Series** — **Appalachian Formations/Groups**

- Stephanian
- Westphalian — D, Bolsov., Duckmantian, Langsettlan
- Namurian

- Upper Pennsylvanian
- Middle Pennsylvanian
- Lower Pennsylvanian

DUNKARD GROUP
- WASHINGTON — 1
- WAYNESBURG A — 1
- WAYNESBURG — 4

MONONGAHELA GROUP
- SEWICKLEY — 16
- REDSTONE — 42
- PITTSBURGH — 43
- LITTLE PITTSBURGH — 1
- ELK LICK — 3

CONEMAUGH GROUP
- HARLEM — 2
- BAKERSTOWN — 11
- BRUSH CREEK — 3
- MAHONING — 3
- UPPER FREEPORT — 13
- UPPER KITTANNING — 4
- MIDDLE KITTANNING — 4
- LOWER KITTANNING — 17

ALLEGHENY GROUP
- NO. 6 BLOCK — 5
- UPPER NO. 5 BLOCK — 8
- NO. 5 BLOCK — 43
- STOCKTON A — 5
- UPPER MERCER — 1
- STOCKTON — 47

KANAWHA FORMATION
- COALBURG — 62
- WINIFREDE — 26
- CHILTON — 1
- LITTLE CHILTON — 2
- FIRE CLAY — 19
- CEDAR GROVE — 12
- WILLIAMSON — 10
- PEERLESS — 16
- NO. 2 GAS — 62
- POWELLTON — 39
- EAGLE — 69
- LITTLE EAGLE — 9
- MATEWAN — 4
- MIDDLE WAR EAGLE — 7
- BENS CREEK — 8
- LOWER WAR EAGLE — 3
- GLENALUM TUNNEL — 4
- GILBERT — 9
- DOUGLAS — 6
- LOWER DOUGLAS — 1
- IAEGER — 3

NEW RIVER FORMATION
- SEWELL B — 1
- SEWELL A — 6
- SEWELL — 53
- WELCH — 5
- BECKLEY — 8
- FIRE CREEK — 12

POCAHONTAS FORMATION
- POCAHONTAS NO. 9 — 1
- POCAHONTAS NO. 8 — 5
- POCAHONTAS NO. 7 — 1
- POCAHONTAS NO. 6 — 12
- POCAHONTAS NO. 5 — 2
- POCAHONTAS NO. 4 — 17
- POCAHONTAS NO. 3R — 1
- POCAHONTAS NO. 3 — 30
- POCAHONTAS NO. 2 — 2

Se scale: 0 1 2 3 4 5 6 7 8 9 10

Updated January 13, 2001 (n=822)

WVGES, 2002

(coals only)

Bulk Analyses

Data provided by REIC

- Acid-base accounting

- Paste pH

- Total organic carbon (TOC)

- Total Se

- Sulfur

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Se by rock type — Total Se Distribution

Se by depth

Se vs. other parameters

Does sulfur predict Se concentrations?

All rock types — scatter plot of Total Se (mg/kg) versus % Sulfur

Coal only — scatter plot of Total Se (mg/kg) versus Pyritic Sulfur (%)

Sulfur is not a good predictor
- Coleman et al. (1993) – Eastern coals
- Neuzil et al. (2005) – Appalachian Plateau coals
- Mullennex (2005) – Southern WV strata

Suggests that not all Se in bound in a sulfide minerals
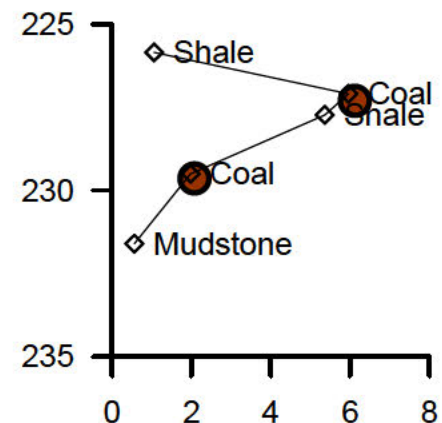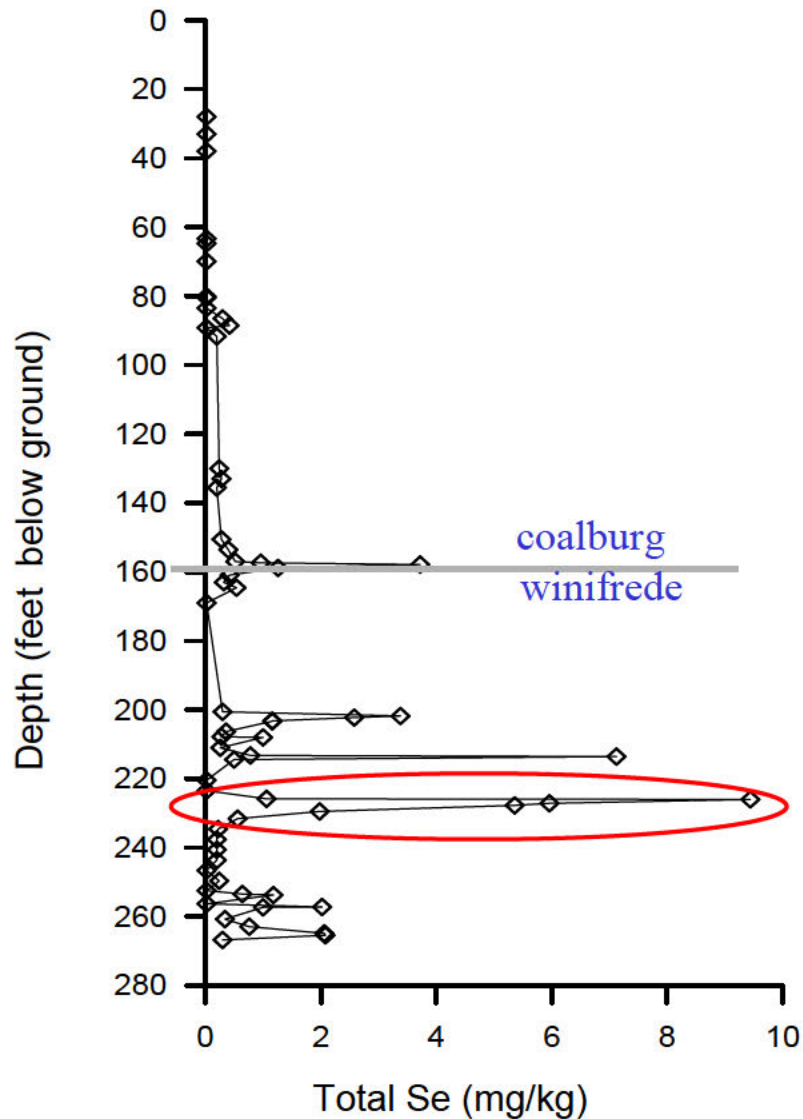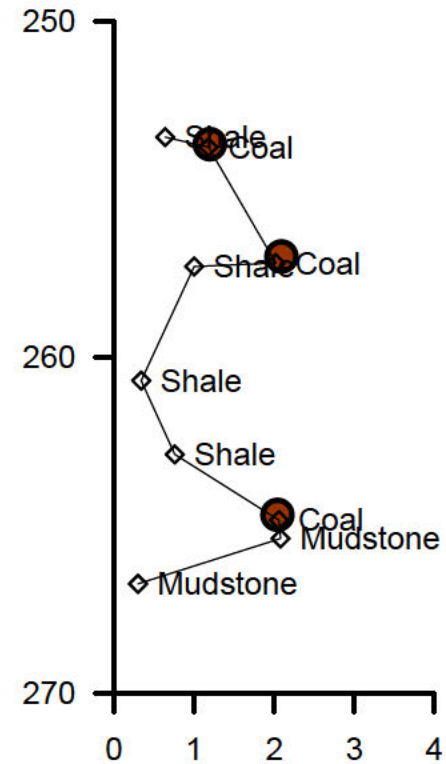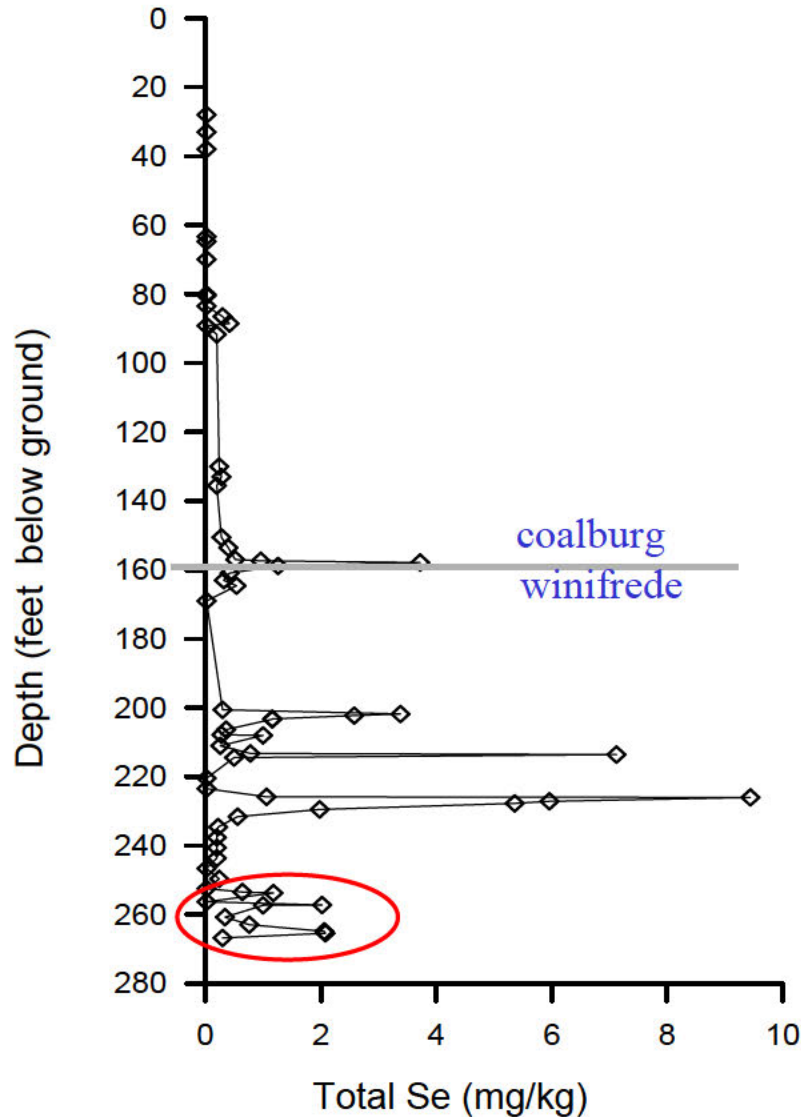
Se vs. other parameters — Total Se Distribution

What seems to work?
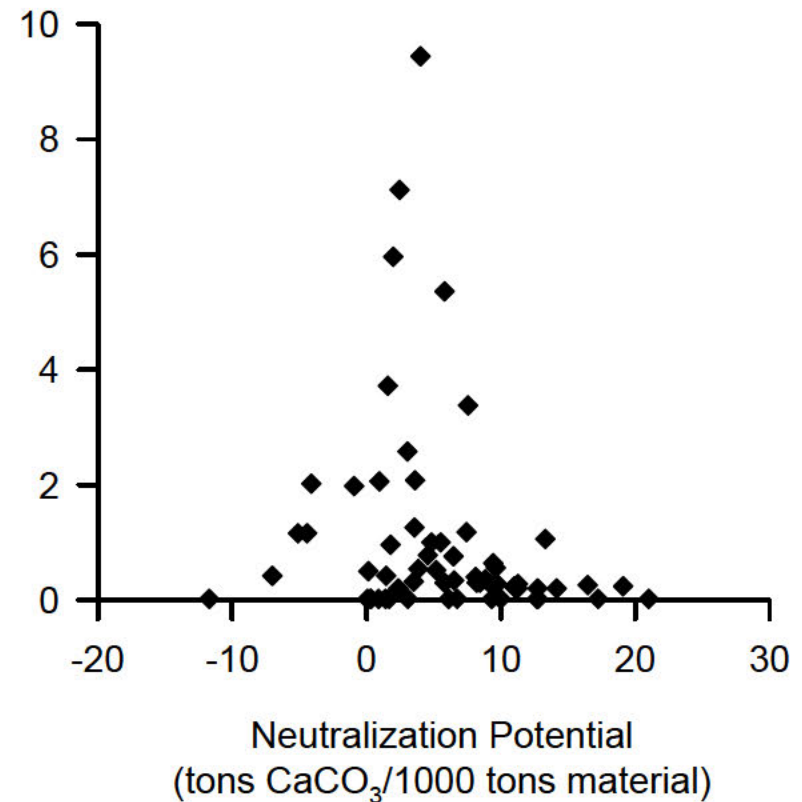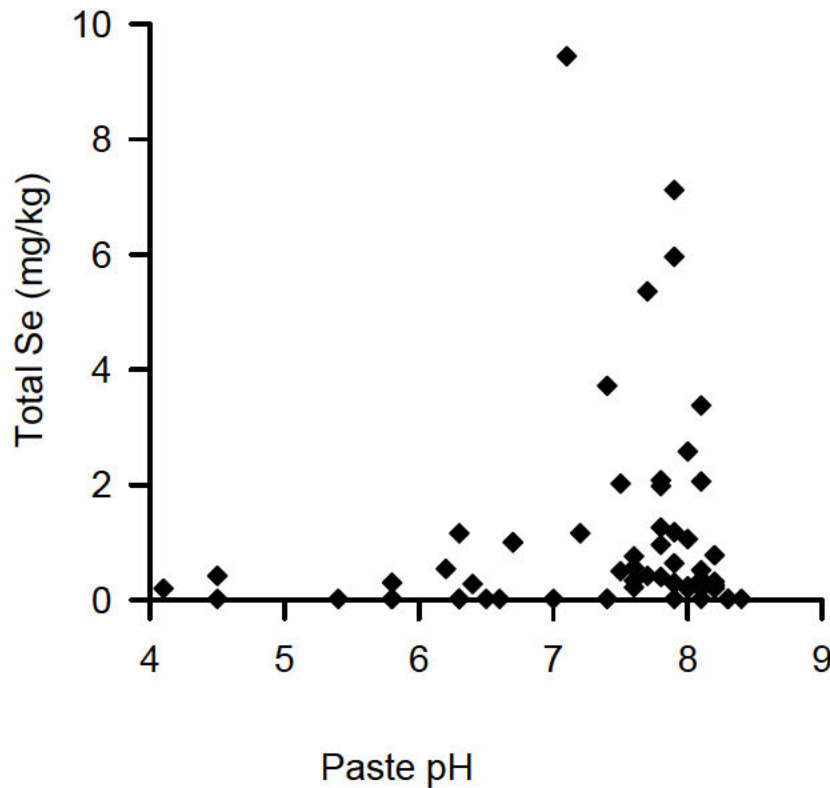
Higher Se conc. more likely to be found in rocks with "neutral characteristics"

Coal-proximate layers

Layers closer to coal – typically have higher Se

But is there a bias by rock type?

Consider a lithology found both close and far from coals

All rock types

Carboliths – high Se, close to coal

Sandstones – low Se, further from coal
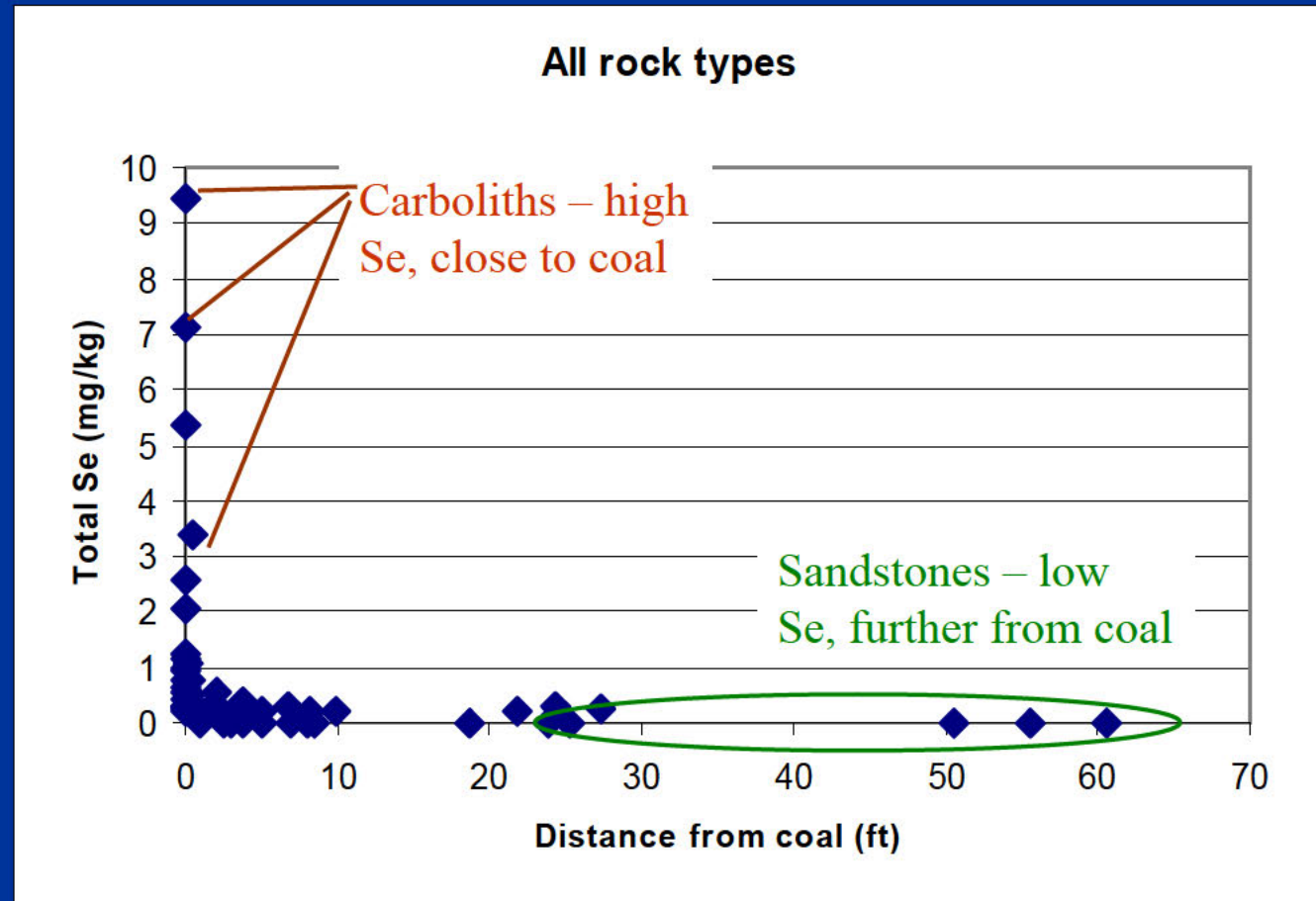
Coal-proximate layers

Same trends for shale and mudstones (34 total)
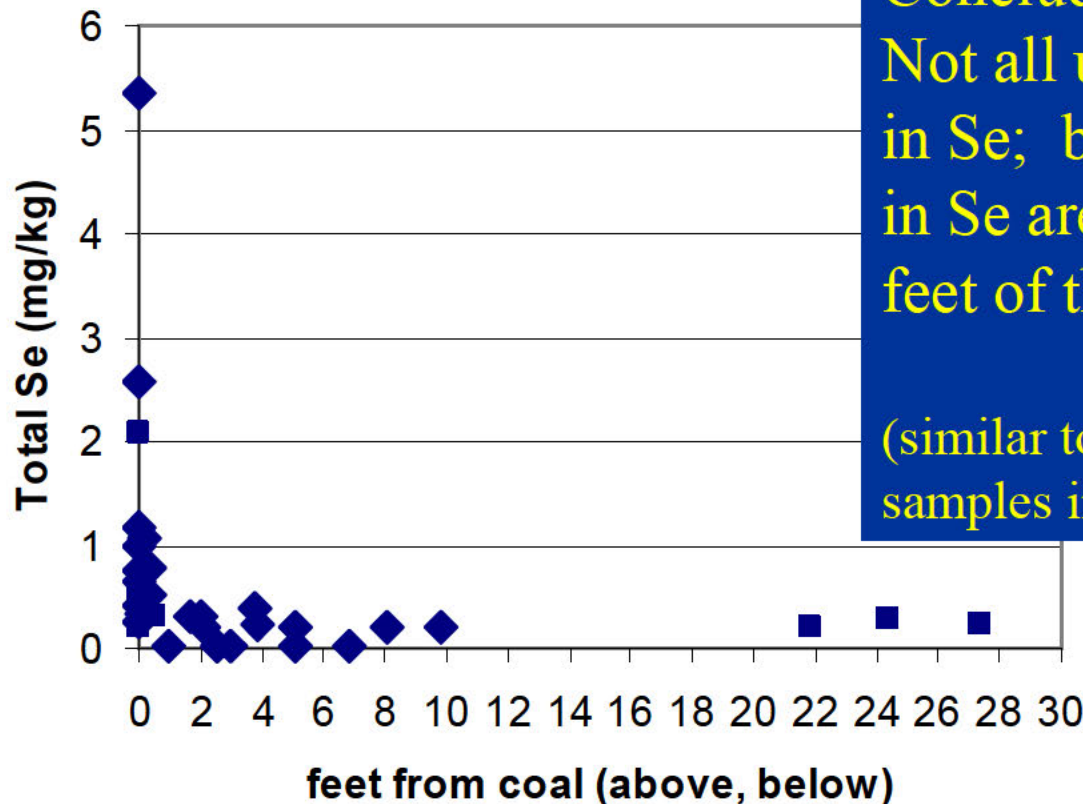
Conclude:
Not all units close to coal are high in Se; but the layers that are high in Se are typically found with two feet of the coals

(similar to Mullennex 2005 - >400 samples in Allegheny & Kanawha Fms)

Outline

- Objectives & Purpose

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- Total Se distribution

- Se mode of occurrence (objective 2)

- Next steps

Modes & Methods

Defined via a reaction with:

Residual

Sulfides

Ascorbic acid + peroxide

Organics

Na Pyrophosphate

Oxide coatings

Hydroxylamine hydrochloride

Exchangeable

Potassium Phosphate

Soluble

De-ionized Water

Modes & Methods

Residual

Sulfides

Organics

Oxide coatings

Exchangeable

Soluble

A few details

- 46 samples

- Duplicate & triplicate

- Process blanks fine

- % recovery good

- Analyzed for total Se (some S)

MEANING

Methods designed to target specific chemical reactions – for determining modes of occurrence

➡️

Not designed to be a direct measure of what would leach in nature

Distribution in coal samples   Se mode of occurrence
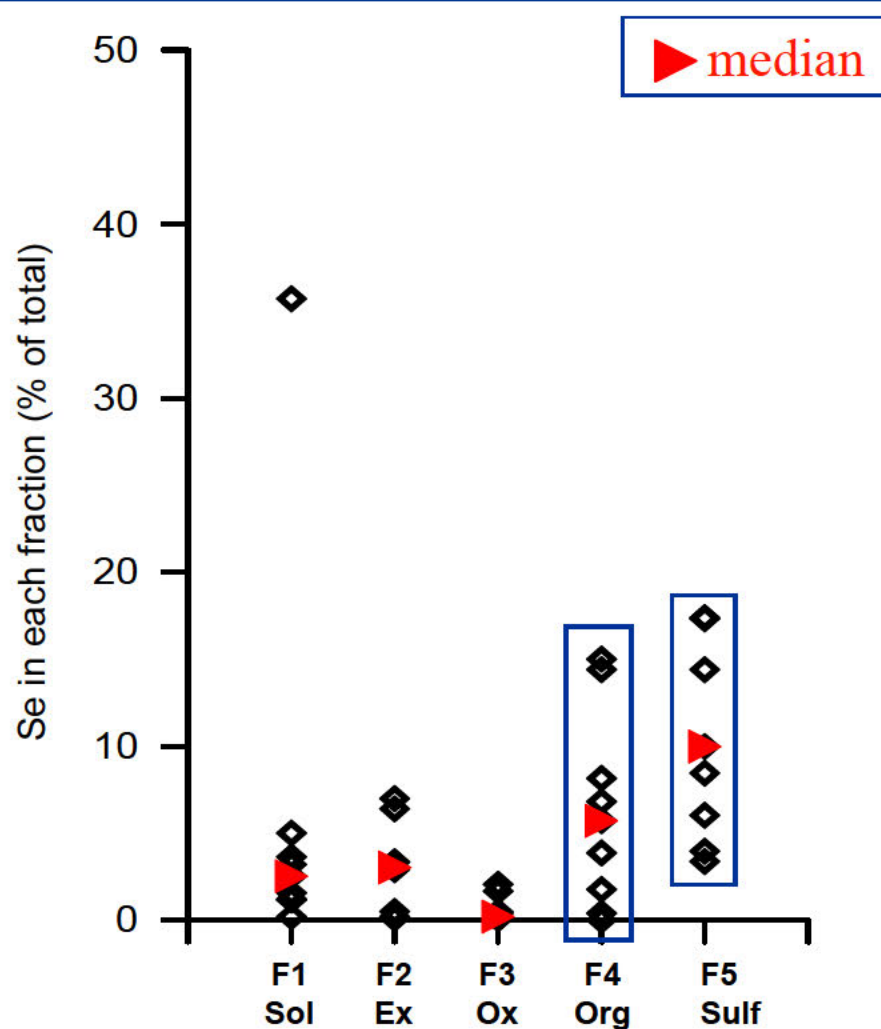
9 coal samples

Regions overlap, but in 8/9 samples there was as much or more Se found in the sulfide than in the organic fraction

Generally, more Se is detected in the sulfide fraction than the organic fraction

Distribution in mudst-shale
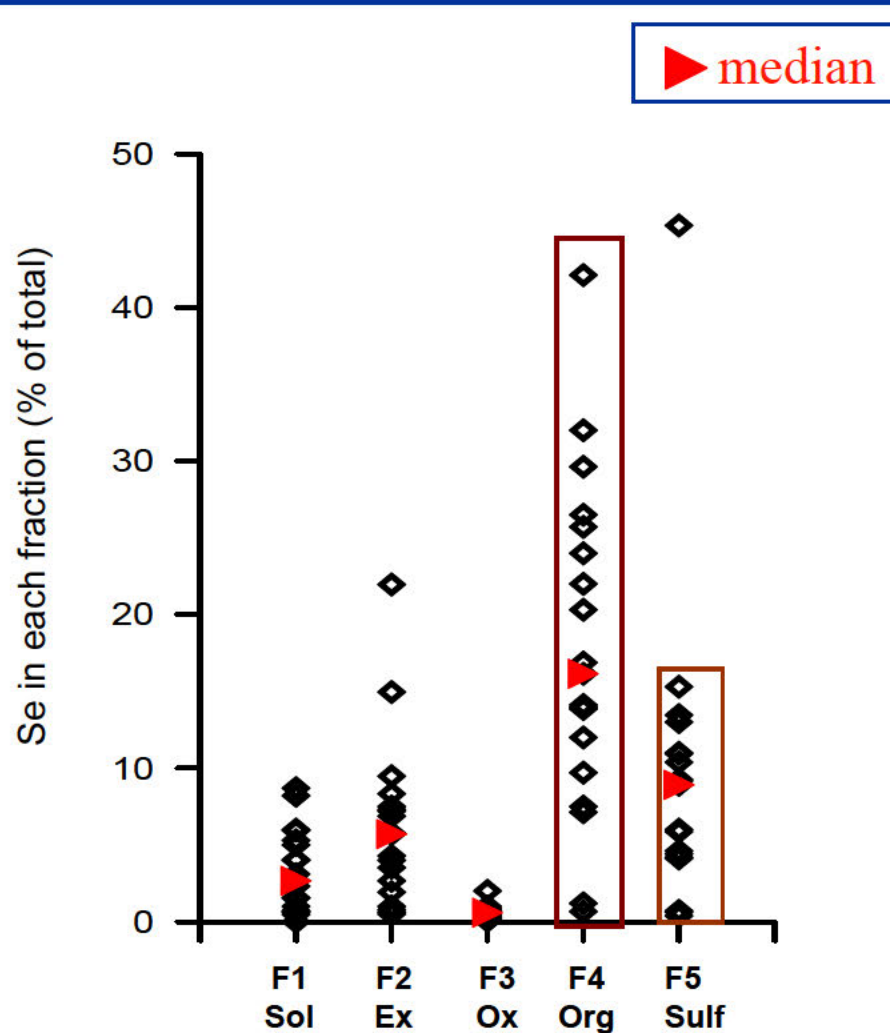
19 samples

Regions overlap, but in 15/19 samples there was as much or more Se found in the organic than in the sulfide fraction

Generally, more Se is detected in the organic fraction than the sulfide fraction

Comparing rock types
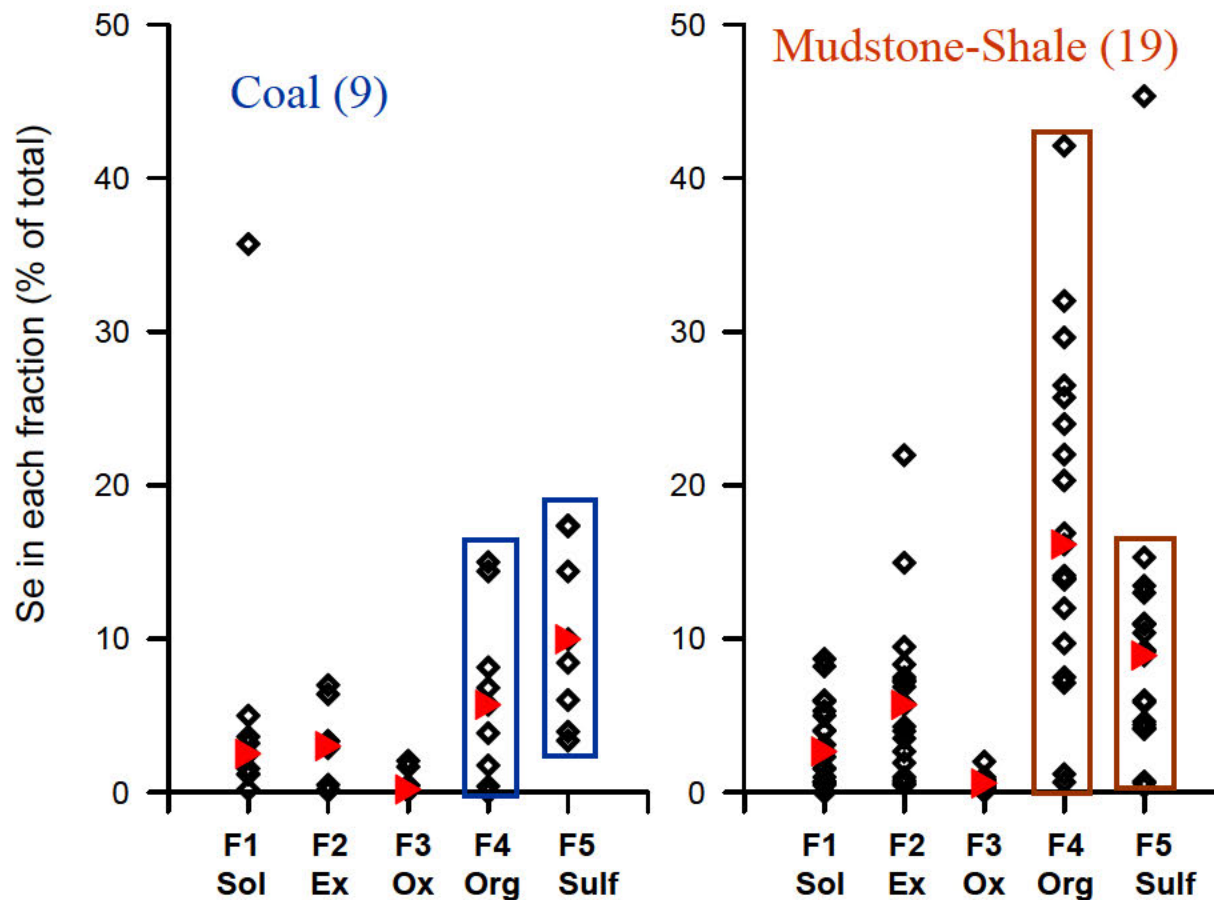
- Both rock types have Se bound in sulfide & organic fractions

- Usually… Sulfide-Se dominates for coal & organic-Se dominates for shales and mudstones

What's left behind?

Coal (9)

Mudstone-Shale (19)
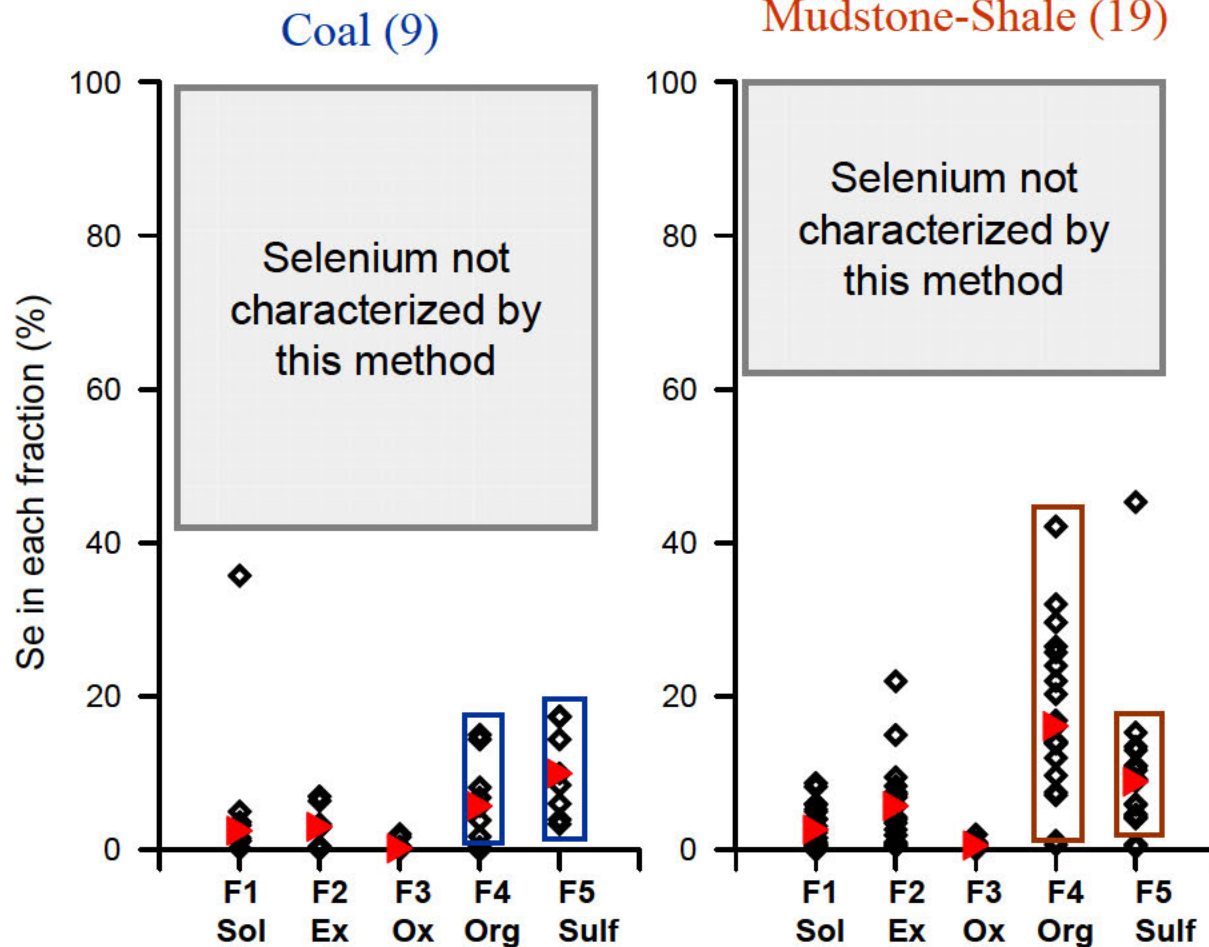
Different y-axis

Is Se in residue generally unavailable? Or is this a function of the test used?

Outline

- Objectives & Purpose

- Project summary

- Total Se distribution

- Se mode of occurrence

- Next steps

Limitations

- Only a single core

- Extraction studies are NOT leaching studies

- Modes of occurrence operationally defined

Total Se

Do the total-Se conclusions apply to a wider area? Compare to:

- Additional cores at site
- Other available data sets

Extract vs. Leach

How do mode-of-occurrence studies compare to leaching tests?

- Conduct both types of studies on the same samples
  - ADTI (Brady, Hornberger) samples
  - Leaching "round robin"

Acknowledgements

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- West Virginia Water Research Institute

- REIC (Tim Keeney)

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THE OCCURRENCE OF SELENIUM IN THE UPPER KANAWHA FORMATION OF THE PENNSYLVANIAN SYSTEM IN THE SOUTHERN WEST VIRGINIA COAL FIELDS

George Jenkins and Nick Schaer
WVDEP

ABSTRACT A search of the literature on selenium reveals that there are little or no studies available on the concentrations of selenium in rock overburden anywhere in the United States. The Environmental Protection Agency's (EPA) concern with the in-stream concentrations of selenium in the Draft Programmatic Environmental Impact Statement conducted in 6 watersheds in West Virginia for mountaintop mining, brought the lack of data on selenium to the attention of West Virginia's Department of Environmental Protection (DEP). To acquire data for a mining National Pollution Discharge Elimination System Permit (NPDES), the DEP's Water Resource section required the drilling of holes to secure data on selenium in the overburden of selected surface mine permits. The results, procedures and conclusions drawn from the initial drilling under this requirement are presented in this paper.

DISCUSSION

The EPA conducted extensive water testing in 6 watersheds in West Virginia in conjunction with the mountaintop mining EIS (*28*). This study was started in 1999 and a draft report on findings is available. In addition to the typical metals that are analyzed for in a surface mine (SMCRA) permit, selenium was noted as a trace metal of concern by the EPA. This concern arose from selenium concentrations in excess of the 5 ppb in-stream chronic water quality limit that exists in West Virginia (*39*). Because the EIS study purposely picked areas that were/are being surface mined in the state, the conclusion has been drawn that surface mining areas, particularly valley fills, are contributing to the selenium concentrations noted. A literature search on selenium revealed that extensive research on selenium in fly ash (Lemly) and soils (Vance) were available, but no papers or research was noted on the concentrations of selenium in rock overburden. This was important to the WVDEP, because we needed to know where the selenium was concentrated on a surface mine job to suggest ways to handle overburden or use other techniques to mine the coal without harming the aquatic environment with toxic selenium, which can cause harm to fish tissue, animals etc. through bio-concentration *30,31,40*). A study by the West Virginia Geologic Survey (WVGS) was posted on the internet that indicated that coal seams of the Upper Kanawha Formation of the Pennsylvanian System (*34,35)* was much higher in selenium than other strata in the coal areas of the Appalachians. The principal mineable seams in this geological section are the Winifrede, Coalburg, Stockton and #5 Block seams.
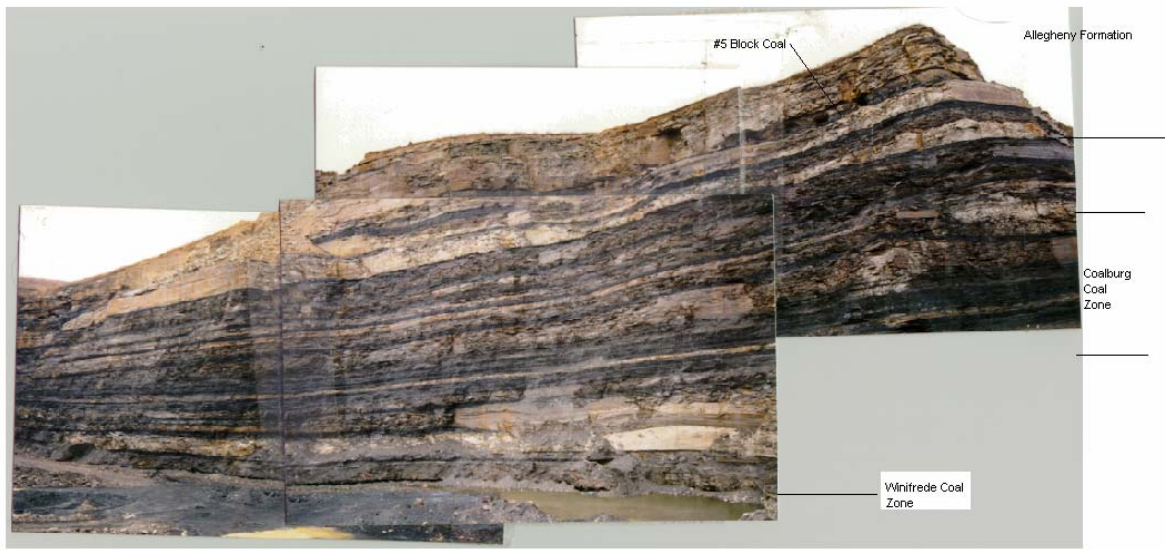
Figure1. Highwall covering the Winifrede to 6-Block coal seams. Picture taken near Sharples, West Virginia at the now inactive Dal-Tex strip mine complex.

 This WVGS study was done by measuring the trace metals in the fly ash of the coal seams that were burned in the state, and back calculating the amount of selenium in the total coal seam. The WVGS study, and other research reviewed, plus conversations with analytical laboratory personnel (*41,42),* indicated that the selenium was associated with organic/carbon based material, like coal seams, carbonaceous shale, etc. Previous work on coal ash and associated materials by one of the authors of this paper for various coal companies also indicated that the coal seams and associated "pit cleanings" (carbonaceous roof, floor and parting material) held the highest concentrations of selenium in the overburden. If the vertical location of the selenium in the "pit cleanings" was correct, then it was possible to design a materials handling plan to isolate this material that would be not cost prohibitive in the mining sequence.

PROTOCOL USED TO ACQUIRE AND ANALYZE THE OVERBURDEN SAMPLES FOR SELENIUM

1. Since 1999, the WVDEP has required that all of the baseline water sites that are submitted for a surface mine permit be tested for trace metals and other compounds, such as phenols, on a one time basis. This data, plus data from several other sources (1.) NPDES renewal Table IV-C analyses. (2.) Data from the Department of Environmental Protection (DEP) trend sites. (3) Data from the EIS in certain watersheds. (4) Data from Water Resources for TMDL's (Total Maximum Daily Loads) etc. (5) and the latest 303(d)

impaired streams list from the Division of Water Resources are checked to see if Selenium or any other metal is above the Title 46-1 State Water Quality Limits (*39*) or of concern.. Any area that has had previous mining and reflects over 5 ppb selenium (current instream chronic water quality standard for selenium) will be selected for drilling to sample the overburden.

2. The drilling will be on approximately 2000' spacing, or other spacing required by the geologist reviewing the surface mining (SMCRA) permit. The holes will be located on the tops of the ridges and drilled down to 10' below the lowest seam to be mined. This will insure that all the overburden to be removed is covered in it's entirety.

3. The core from the drilling will be broken down into vertical sections of 5' or less if the strata type changes. The object is to break the core down into small recognizable sections that can be separated by high selenium content in the mining sequence. This breakdown will also mirror the acid/base testing breakdown, which has been used for decades in surface mining in WV.

4. Each 5' or less section is then analyzed for total selenium by the 3050B (for Acid digestion of Solids) method. Any strata that has a total selenium concentration of 1mg/kg (*25,33,36*) or greater is considered potentially toxic and will have to undergo further testing or an encapsulation/isolation plan provided to deal with the selenium laden overburden.

5. There are several leachate tests available for the next level, if the applicant does not want to do the materials handling plan based on the total selenium analyses. They are (1) Column Leaching (2) Soxhlet (3) Phosphate(*25*)etc. Any leachate test that results in a reading of greater that 5 ug/kg will be considered toxic for selenium and will be included in a specific materials handling plan.

RESULTS FROM DRILLING IN LOGAN AND MINGO COUNTIES IN SOUTHERN WEST VIRGINIA

The protocol was applied to 3 mining areas in the spring of 2004. The results of 1 hole from northern Logan County, 5 holes from southern Logan County and 1 hole from Mingo County (locations shown in figure 2) are included in this report. All of these drilling areas were or are going to be mountaintop mined for the Coalburg and above/Upper Kanawha strata The cross section of the Phoenix #4 area in southern Logan County, and the drill logs with selenium content in the other two areas indicate that the selenium is concentrated in the "pit cleanings" as theorized at the beginning of the study. These "pit cleanings" are the immediate dark shale roof of the Coalburg, Stockton and Five Block coal seams, partings in the coal seams and sometimes the immediate floor of the coal seams. These strata exhibit selenium concentrations of almost one order of magnitude above the background concentrations of selenium in the sandstones, limestones and other strata encountered in the mining sequence. That is .05 to .25 mg/kg in the sandstones and .5 to 1+ mg/kg in the carbonaceous shales, coal partings, floor of the coal seam and the seam itself (see Table 1). The potentially toxic selenium concentrations of 1mg/kg and above are almost solely concentrated in the coal seams, partings and roof and floor of the seams to be mined. Leachate tests on these holes are in

progress and could be the subject of a follow-up paper. The current results definitively indicate that the selenium has an affinity for organic material in the overburden column.

Selenium Overbuden Sites
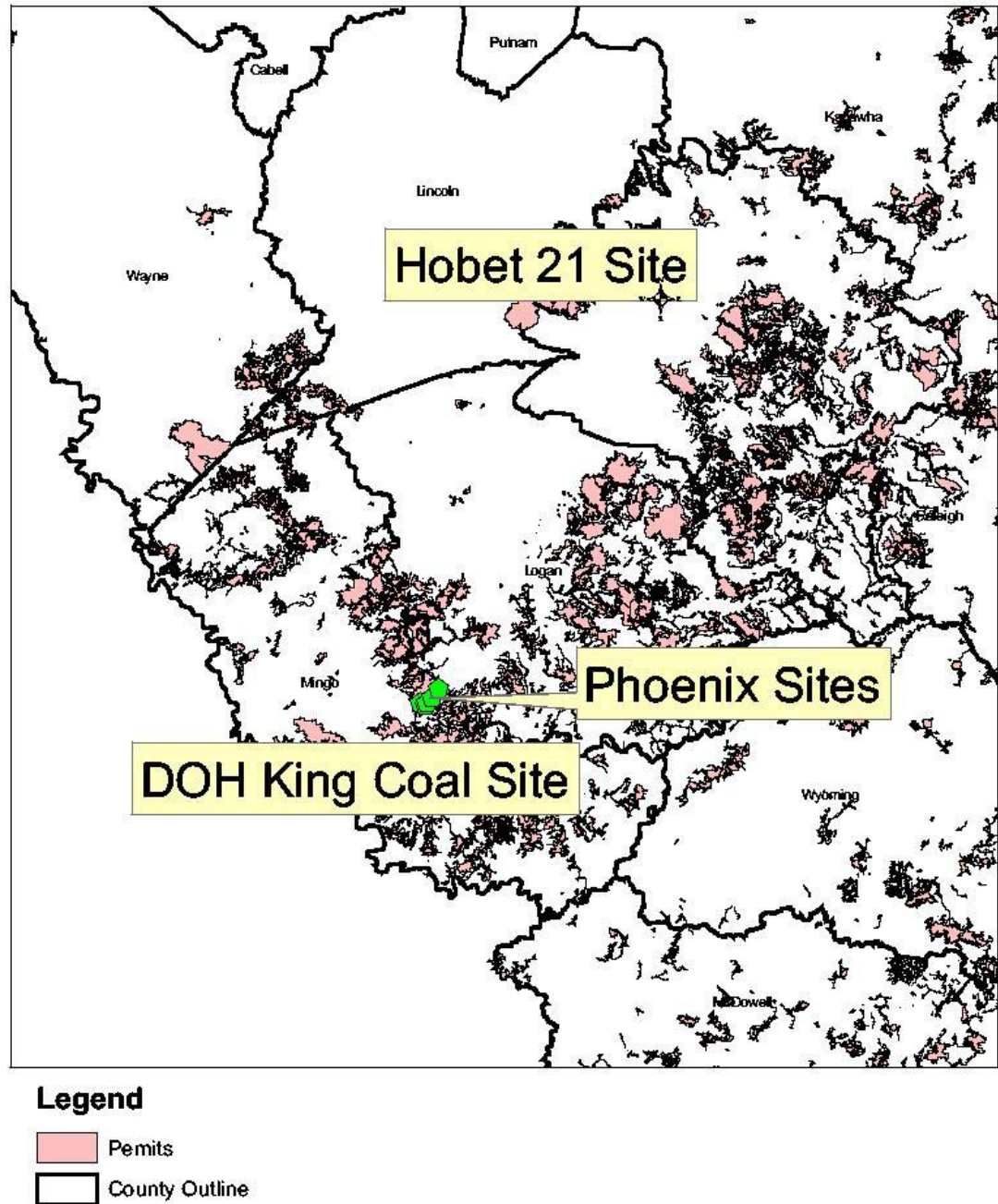
Figure 2. Location of selenium overburden sampling in southern West Virginia.

RECOMMENDED MATERIALS HANDLING PLAN

1. Because the toxic selenium material that needs to be isolated is concentrated in small vertical zones that have to be set aside to recover the coal seam, and the material is a black/dark gray material that is visibly differentiated in the field, the mining company can split this material out in the coal pits. (see figure 3).

Figure 3. #5 Block coal and other black "Pit Cleanings" gathered in piles for removal to special handling areas. Pen Coal strip mine in Wayne County, West Virginia.

2. It is important to rip up 6" to 1' of the floor of the bottom coal seam so that no selenium laden material is left to contaminate the water/rock interface.
3. The toxic material should be removed to an area on the job that is high and dry away from water courses, and under no circumstance should any of this material be put in a valley fill.
4. The material should then be put on a free draining pad of @10' of coarse non-selenium laden material and covered with at least 4' of the most impervious material on the surface mine job. This method will keep water from leaching through the selenium laden overburden.

CONCLUSIONS

It is apparent from the analytical results and research to date that the selenium is concentrated in the "pit cleanings" and particularly in the Upper Kanawha strata in West Virginia. The cut-off of 1 mg/kg limit for identifying the material that has to

undergo further leachate testing looks valid in differentiating the high selenium material to be isolated from the lower concentration material. The visual difference of the black /darker selenium laden material from the other overburden in the Upper Kanawha series is very useful in separating the toxic material from the non-toxic in the field. Further work needs to be done on the different methods of leachate tests to calculate what percentage of selenium in the overburden will be mobilized into the hydrologic environment. Also, it is imperative that a study of how selenium is dispersed in flowing streams versus standing bodies of water is critical to the understanding of what impact selenium may have to the aquatic environment. The moral to the story is to isolate the black/darker selenium laden material and to keep any of this material from the valley fills. This material, besides having high concentrations of selenium, is also typically high in iron and manganese and other trace metals, as well as more acidic, so that the materials handling plan suggested will pay extra dividends.

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40. Participation of both authors in the Federal and State Interagency meetings on Selenium in April 2004 at Charleston, WV.

41. Private conversations with John Sturm of Sturm Environmental Services, Anmoore, WV

42. Private conversations with personnel at REIC laboratories, Beckley, WV

Table 1. Sample Selenium Data from Phoenix Coal site shown in figure 2. Data from core PX-04-10. REIC Job#: 0405081

SAMPLE NUMBER	SAMPLE INTERVAL	THICKNESS (feet)	ROCK TYPE	SELENIUM (mg/kg)
1	23.00-27.50	4.50	Sandstone	ND
2	43.00-45.00	2.00	Sandstone	ND
3	45.00-45.90	0.90	Shale	0.82
4	45.90-46.15	0.25	Coal	0.94
5	46.40-46.65	0.25	Shale	2.74
6	**46.65-51.25**	**4.60**	**Coal**	**1.14**
7	51.25-52.20	0.95	Shale/Sandstone	1.80
8	52.20-57.00	4.80	Sandstone	ND
9	57.00-62.00	5.00	Sandstone	ND
10	62.00-67.00	5.00	Sandstone	ND
11	67.00-72.00	5.00	Sandstone	ND
12	72.00-77.00	5.00	Sandstone	ND
13	77.00-82.00	5.00	Sandstone	ND
14	82.00-87.00	5.00	Sandstone	ND
15	87.00-92.00	5.00	Sandstone	ND
16	92.00-95.70	3.70	Sandstone	ND
17	95.70-96.60	0.90	Sandstone/ Mudstone/ Coal	0.40
18	96.60-99.75	3.15	Sandstone	0.20
19	99.75-100.30	0.55	Shale	0.34
20	**100.30-101.80**	**1.59**	**Coal**	**0.48**
21	101.80-102.30	0.50	Mudstone	2.28*
22	102.30-105.00	2.70	Shale	0.42
23	105.00-108.00	3.00	Shale	0.20
24	108.00-111.00	3.00	Shale	0.24
25	111.00-114.00	3.00	Shale	0.36
26	114.00-117.00	3.00	Shale	0.36
27	117.00-120.00	3.00	Shale	0.46
28	120.00-123.00	3.00	Shale	0.40
29	123.00-125.00	2.00	Shale	0.44
30	125.00-126.95	1.95	Shale	0.38
31	126.95-129.30	2.35	Shale	1.32
32	129.30-129.50	0.20	Shale	2.12
33	129.50-131.03	1.53	Coal	1.82
SAMPLE NUMBER	SAMPLE INTERVAL	THICKNESS (feet)	ROCK TYPE	SELENIUM (mgflcg)
34	131.03-131.37	0.34	Shale/Coal	3.00

35	131.37-131.70	0.33	Coal	1.90
36	131.70-132.90	1.20	Shale	0.82
37	132.90-135.00	2.10	Mudstone/ Shale	ND
38	135.00-137.00	2.00	Sandstone/ Mudstone	0.20
39	137.00-139.85	2.85	Shale	0.54
40	139.85-140.60	0.75	Shale/Coal	2.60
41	140.60-141.60	1.00	Coal	5.08
42	141.60-143.00	1.40	Mudstone	1.48
43	143.00-146.00	3.00	Mudstone	ND
44	146.00-149.35	3.35	Sandstone	ND
45	149.35-150.40	1.05	Shale	ND
46	150.40-155.00	4.60	Sandstone	ND
47	155.00-160.00	5.00	Sandstone	ND
48	160.00-165.00	5.00	Sandstone	ND
49	165.00-170.00	5.00	Sandstone	ND
50	170.00-175.00	5.00	Sandstone	ND
51	175.00-180.00	5.00	Sandstone	ND
52	180.00-183.65	3.65	Sandstone	ND
53	183.65-184.50	0.85	Shale/Sandstone	ND
54	184.50-189.00	4.50	Sandstone	ND
55	189.00-194.00	5.00	Sandstone	ND
56	194.00-199.00	5.00	Sandstone	ND
57	199.00-204.00	5.00	Sandstone	ND
58	204.00-209.00	5.00	Sandstone	ND
59	209.00-213.00	4.00	Sandstone	0.30
60	213.00-217.00	4.00	Sandstone	ND
61	217.00-220.20	3.20	Mudstone/Sandstone	0.32
62	220.20-225.00	4.80	Sandstone	ND
63	225.00-230.00	5.00	Sandstone	ND
64	230.00-235.00	5.00	Sandstone	ND
65	235.00-240.00	5.00	Sandstone	ND
66	240.00-244.90	4.90	Sandstone	ND
67	244.90-248.60	3.70	Sandstone	ND
68	248.60-250.70	2.10	Sandstone	1.26
69	250.70-251.64	0.94	Coal	3.98
70	251.64-253.10	1.46	Coal	1.60
71	253.10-253.55	0.45	Carbolith	2.64
72	253.55-254.46	0.91	Carbolith/Coal	2.66

SAMPLE NUMBER	SAMPLE INTERVAL	THICKNESS (feet)	ROCK TYPE	SELENIUM (mg/kg)
73	254.46-254.93	0.47	Coal	2.80
74	254.93-256.45	1.52	Coal	2.54

SAMPLE NUMBER	SAMPLE INTERVAL	THICKNESS (feet)	ROCK TYPE	SELENIUM (mg/kg)
75	256.45-257.05	0.60	Shale	3.28
76	257.05-260.00	2.95	Sh	0.62
77	260.00-260.85	0.85	Shale/Coal	2.38
78	260.85-261.15	0.30	Coal	1.20
79	261.15-261.45	0.30	Carbolith	1.40
80	261.45-263.50	2.05	Coal	0.92
81	263.50-264.25	0.75	Shale	0.62
82	264.25-267.10	2.85	Shale	0.28
83	267.10-269.95	2.85	Shale	ND
84	269.95-271.95	2.00	Sandstone/ Shale	0.26
85	271.95272.41	0.46	Coal	1.86
86	272.41-274.10	1.69	Shale	0.26
87	274.10-277.00	2.90	Mudstone	ND
88	277.00-280.00	3.00	Sandstone/Shale	ND
89	280.00-283.00	3.00	Shale	ND
90	283.00-285.50	2.50	Shale	0.38
91	**285.50-285.92**	**0.42**	Coal	**1.60**
92	**285.92-286.15**	**0.23**	Carbolith	**8.64**
93	**286.15-287.55**	**1.40**	Coal	**2.10**
94	287.55-287.75	0.20	Shale	0.76
95	287.75-293.00	5.25	Sandstone	0.20
96	293.00-298.00	5.00	Sandstone	ND
97	298.00-303.00	5.00	Sandstone	ND
98	303.00-308.00	5.00	Sandstone	ND
99	308.00-313.00	5.00	Sandstone	ND

ND - Not Detected at the MDL of 0.2 mg/kg.

* - The matrix spike for selenium exceeded method control limits due to matrix interference.

Matthew Klasen/DC/USEPA/US
01/07/2011 01:54 AM

To   Matthew Klasen

cc

bcc

Subject   Current

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780

cell (202) 380-7229 ☐ - 2011-01-06 Compiled H&W RD Comment Responses.docx ☐ - 2011-01-06 Compiled WVDEP RD Comment Responses.doc

ATTACHMENTS REDACTED - DELIBERATIVE

Matthew
Klasen/DC/USEPA/US

01/07/2011 09:24 AM

To   Christopher Hunter

cc

bcc

Subject   Current RD RTC draft (WVDEP and H&W) for verifying FD
changes were made

Here it is (both WVDEP and the main body) for reviewing the "verify change to FD" comments. As you
know, Kevin doesn't have all of these yet (181-242) so I'll send you those later.

I think what's easiest for version control is for you to just make a running list of the things you've confirmed
are in the FD or appendices, and then send that to me so I can delete the comments in the compiled
versions. Does that work?

Thanks,
Matt   ATTACHMENTS REDACTED – DELIBERATIVE

2011-01-06 Compiled WVDEP RD Comment Responses.doc   2011-01-06 Compiled H&W RD Comment Responses.docx

----

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229

**Stefania
Shamet/R3/USEPA/US**

01/07/2011 09:43 AM

To   Matthew Klasen

cc

bcc

Subject   180-242

Other than the ones I've identified

ATTACHMENT REDACTED – DELIBERATIVE

2011-01-02 Compiled H&W RD Comment Responsessds.docx

Nancy Stoner/DC/USEPA/US

01/07/2011 10:01 AM

To "Greg Peck"

cc

bcc

Subject Fw: Spruce "Fact Sheet"

If you print me a copy, I will. I'm in my office, thx
  Gregory Peck

  ----- Original Message -----
    From: Gregory Peck
    Sent: 01/07/2011 09:20 AM EST
    To: Matthew Klasen; Karyn Wendelowski; Kevin Minoli; Nancy Stoner
    Subject: Spruce "Fact Sheet"

It would be great if a couple of key people could take a quick look at this 2 page Fact Sheet and let me know your thoughts before I distribute more broadly. We'll need this for the discussion with Bob at 1pm this afternoon - but don't distract yourselves from other Spruce priorities.

Thanks

ATTACHMENT REDACTED - DELIBERATIVE

Mining Draft Spruce Fact Sheet JAN 07 11.doc

Denise Keehner/DC/USEPA/US

01/07/2011 10:22 AM

To Nancy Stoner, Gregory Peck

cc

bcc

Subject Fw: Revised Executive Summary

Latest iteration.

From:	David Evans/DC/USEPA/US
To:	Denise Keehner/DC/USEPA/US@EPA
Cc:	Benita Best-Wong/DC/USEPA/US@EPA, Jim Pendergast/DC/USEPA/US@EPA, Brian Frazer/DC/USEPA/US@EPA, Lynda Hall/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Julia McCarthy/R8/USEPA/US@EPA
Date:	01/06/2011 12:59 PM
Subject:	Revised Executive Summary

Denise,

Attached below is a comprehensively revised/substantively expanded draft of the Spruce Veto Executive Summary. All credit to Julia and Chris; Brian and I have reviewed and fully endorse this version.

Look forward to your feedback, questions, comments.

Dave

David Evans, Director
Wetlands Division
Office of Wetlands, Oceans and Watersheds
(202) 566-0535

From:	Christopher Hunter/DC/USEPA/US
To:	Brian Frazer/DC/USEPA/US@EPA, David Evans/DC/USEPA/US@EPA
Cc:	Julia McCarthy/R8/USEPA/US@EPA
Date:	01/06/2011 11:03 AM
Subject:	Revised Executive Summary

Dave and Brian,
attached is the revised executive summary, as requested by Nancy. This version includes your comments. Please review and forward to Denise.

Thanks,
Chris

ATTACHMENT REDACTED - DELIBERATIVE

Revised Spruce 404c Executive Summary.doc

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

Marcel	To	Carrie Traver
Tchaou/DC/USEPA/US	cc	Christopher Hunter
01/07/2011 11:12 AM	bcc	
	Subject	Fw: Info for Lemly (2006) and West Virginia Collection Permit database citation -- Fw: IMPORTANT correction - Fw: Lemley quote that needs citation/reference verification in Appendices and FD & RD

Carrie,
I am checking with you to make sure that the issue addressed in the email below is taken care of. I did not do anything with it on my end. Please advise

****
Marcel K. Tchaou, Ph.D., P.E., P.H.
Environmental Engineer
Wetlands & Aquatic Resources Regulatory Branch
Office of Wetlands, Oceans and Watersheds
U.S. EPA
1200 Pennsylvania Avenue, NW (MC 4502T)
Washington, DC 20460
202-566-1904

----- Forwarded by Marcel Tchaou/DC/USEPA/US on 01/07/2011 11:10 AM -----

From:	Frank Borsuk/R3/USEPA/US
To:	Carrie Traver/R3/USEPA/US@EPA, Marcel Tchaou/DC/USEPA/US@EPA
Cc:	Margaret Passmore/R3/USEPA/US@EPA, Louis Reynolds/R3/USEPA/US@EPA
Date:	01/06/2011 12:30 PM
Subject:	Info for Lemly (2006) and West Virginia Collection Permit database citation -- Fw: IMPORTANT correction - Fw: Lemley quote that needs citation/reference verification in Appendices and FD & RD

Carrie/Marcel:

(b) (5)

Frank

Frank Borsuk, Ph.D.
Aquatic/Fisheries Biologist
Freshwater Biology Team
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Office of Monitoring & Assessment (3EA50)
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Please visit our website at http://epa.gov/reg3esd1/3ea50.htm

----- Forwarded by Frank Borsuk/R3/USEPA/US on 01/06/2011 12:15 PM -----

From:	Frank Borsuk/R3/USEPA/US
To:	Margaret Passmore/R3/USEPA/US@EPA, Regina Poeske/R3/USEPA/US@EPA
Cc:	borsuk.frank@epa.gov
Date:	12/13/2010 04:43 PM
Subject:	IMPORTANT correction - Fw: Lemley quote that needs citation/reference verification in Appendices and FD & RD

(b) (5), (b) (6)

Frank

Please visit our website at http://epa.gov/reg3esd1/3ea50.htm   palmer_etal_2010_mountaintop.pdf

SCIENCE AND REGULATION

Mountaintop Mining Consequences

Damage to ecosystems and threats to human health and the lack of effective mitigation require new approaches to mining regulation.

M. A. Palmer,[1,2] E. S. Bernhardt,[3] W. H. Schlesinger,[4] K. N. Eshleman,[1] E. Foufoula-Georgiou,[5] M. S. Hendryx,[6] A. D. Lemly,[7] G. E. Likens,[4] O. L. Loucks,[8] M. E. Power,[9] P. S. White,[10] P. R. Wilcock[11]

There has been a global, 30-year increase in surface mining (1), which is now the dominant driver of land-use change in the central Appalachian ecoregion of the United States (2). One major form of such mining, mountaintop mining with valley fills (MTM/VF) (3), is widespread throughout eastern Kentucky, West Virginia (WV), and southwestern Virginia. Upper elevation forests are cleared and stripped of topsoil, and explosives are used to break up rocks to access buried coal (fig. S1). Excess rock (mine "spoil") is pushed into adjacent valleys, where it buries existing streams.

Despite much debate in the United States (4), surprisingly little attention has been given to the growing scientific evidence of the negative impacts of MTM/VF. Our analyses of current peer-reviewed studies and of new water-quality data from WV streams revealed serious environmental impacts that mitigation practices cannot successfully address. Published studies also show a high potential for human health impacts.

Ecological Losses, Downstream Impacts

The extensive tracts of deciduous forests destroyed by MTM/VF support some of the highest biodiversity in North America, including several endangered species. Burial of headwater streams by valley fills causes permanent loss of ecosystems that play critical roles in ecological processes such as nutrient cycling and production of organic matter for downstream food webs; these small Appalachian streams also support abundant aquatic organisms, including many endemic species (5). Many studies show that when more than 5 to 10% of a watershed's area is affected by anthropogenic activities, stream biodiversity and water quality suffer (6, 7). Multiple watersheds in WV

already have more than 10% of their total area disturbed by surface mining (table S1).

Hydrologic flow paths in Appalachian forests are predominantly through permeable soil layers. However, in mined sites, removal of vegetation, alterations in topography, loss of topsoil, and soil compaction from use of heavy machinery reduce infiltration capacity and promote runoff by overland flow (8). This leads to greater storm runoff and increased frequency and magnitude of downstream flooding (9, 10).

Water emerges from the base of valley fills containing a variety of solutes toxic or damaging to biota (11). Declines in stream biodiversity have been linked to the level of mining disturbance in WV watersheds (12). Below valley fills in the central Appalachians, streams are characterized by increases in pH, electrical conductivity, and total dissolved solids due to elevated concentrations of sulfate (SO_4), calcium, magnesium, and bicarbonate ions (13). The ions are released as coal-generated sulfuric acid weathers carbonate rocks. Stream water SO_4 concentrations are closely linked to the extent of mining in these watersheds (11, 14). We found that significant linear increases in the concentrations of metals, as well as decreases in multiple measures of biological health, were associated with increases in stream water SO_4 in streams below mined sites (see the chart on page 149). Recovery of biodiversity in mining waste-impacted streams has not been documented, and SO_4 pollution is known to persist long after mining ceases (14).

Conductivity, and concentrations of SO_4 and other pollutants associated with mine runoff, can directly cause environmental degradation, including disruption of water and ion balance in aquatic biota (12). Elevated SO_4 can exacerbate nutrient pollution of downstream rivers and reservoirs by increasing

nitrogen and phosphorus availability through internal eutrophication (15, 16). Elevated SO_4 can also increase microbial production of hydrogen sulfide, a toxin for many aquatic plants and organisms (17). Mn, Fe, Al, and Se can become further concentrated in stream sediments, and Se bioaccumulates in organisms (11) (figs. S1 and S2).

A survey of 78 MTM/VF streams found that 73 had Se water concentrations greater than the $2.0\,\mu g$/liter threshold for toxic bioaccumulation (18). Se levels exceed this in many WV streams (see the chart on page 149). In some freshwater food webs, Se has bioaccumulated to four times the toxic level; this can cause teratogenic deformities in larval fish (fig. S2) (19), leave fish with Se concentrations above the threshold for reproductive failure (4 ppm), and expose birds to reproductive failure when they eat fish with Se >7 ppm (19, 20). Biota may be exposed to concentrations higher than in the water since many feed on streambed algae that can bioconcentrate Se as much as 800 to 2000 times that in water concentrations (21).

Potential for Human Health Impacts

Even after mine-site reclamation (attempts to return a site to premined conditions), groundwater samples from domestic supply wells have higher levels of mine-derived chemical constituents than well water from unmined areas (22). Human health impacts may come from contact with streams or exposure to airborne toxins and dust. State advisories are in effect for excessive human consumption of Se in fish from MTM/VF affected waters. Elevated levels of airborne, hazardous dust have been documented around surface mining operations (23). Adult hospitalizations for chronic pulmonary disorders and hypertension are elevated as a function of county-level coal production, as are rates of mortality; lung cancer; and chronic heart, lung, and kidney disease (24). Health problems are for women and men, so effects are not simply a result of direct occupational exposure of predominantly male coal miners (24).

Mitigation Effects

Reclamation of MTM/VF sites historically has involved planting a few grass and herb species (20, 25). Compared with unmined

[1]University of Maryland Center for Environmental Science, Cambridge, MD 21613, USA. [2]University of Maryland, College Park, MD 20742, USA. [3]Duke University, Durham, NC 27708, USA. [4]Cary Institute of Ecosystem Studies, Millbrook, NY 12545, USA. [5]University of Minnesota, Minneapolis, MN 55414, USA. [6]West Virginia University, Morgantown, WV 26506, USA. [7]Wake Forest University, Winston Salem, NC 27109, USA. [8]Miami University, Oxford, OH 45056, USA. [9]University of California at Berkeley, Berkeley, CA 94720, USA. [10]University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA. [11]Johns Hopkins University, Baltimore, MD 21218, USA.

*Author for correspondence. E mail: mpalmer@umd.edu
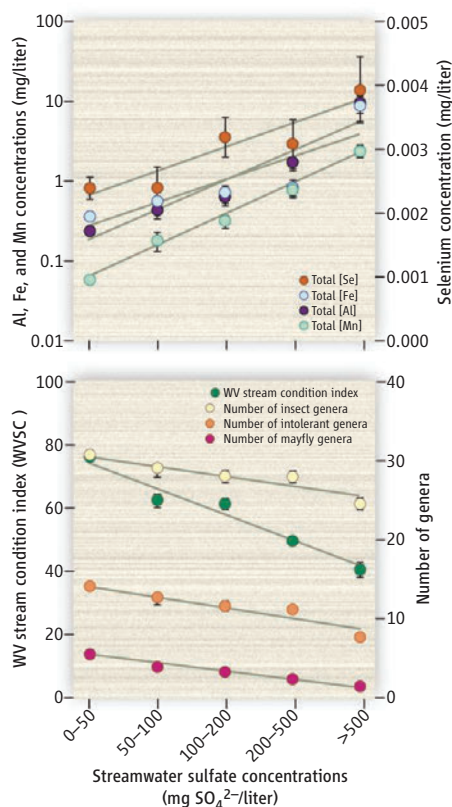
Mining effects on stream chemistry and biota. Sulfate concentrations reflect amount of mining in watershed. (**Top**) Average concentrations of manganese, iron, aluminum, and selenium. (**Bottom**) Stream invertebrate community metrics in relation to sulfate concentrations for 1058 WV streams (methods in table S2). Regressions all statistically significant (table S3).

sites, reclaimed soils characteristically have higher bulk density, lower organic content, low water-infiltration rates, and low nutrient content (8, 25). Many reclaimed areas show little or no regrowth of woody vegetation and minimal carbon (C) storage even after 15 years (26). Decreased forest productivity may be related to the type of surface material (e.g., brown versus gray sandstone) used in the reclamation (27). In reclaimed forests, projected C sequestration after 60 years is only about 77% of that in undisturbed vegetation in the same region (28). Mined areas planted to grassland sequester much less. Since reclamation areas encompass >15% of the land surface in some regions (29) (table S1), significant potential for terrestrial C storage is lost.

Mitigation plans generally propose creation of intermittently flowing streams on mining sites and enhancement of streams off-site. Stream creation typically involves building channels with morphologies similar to unaffected streams; however, because they are on or near valley fills, the surrounding topography, vegetation, soils, hydrology, and

water chemistry are fundamentally altered from the premining state. U.S. rules have considered stream creation a valid form of mitigation while acknowledging the lack of science documenting its efficacy (30). Senior officials of the U.S. Army Corps of Engineers (ACOE) have testified that they do not know of a successful stream creation project in conjunction with MTM/VF (31).

A Failure of Policy and Enforcement
The U.S. Clean Water Act and its implementing regulations state that burying streams with materials discharged from mining should be avoided. Mitigation must render nonsignificant the impacts that mining activities have on the structure and function of aquatic ecosystems. The Surface Mining Control and Reclamation Act imposes requirements to minimize impacts on the land and on natural channels, such as requiring that water discharged from mines will not degrade stream water quality below established standards.

Yet mine-related contaminants persist in streams well below valley fills, forests are destroyed, headwater streams are lost, and biodiversity is reduced; all of these demonstrate that MTM/VF causes significant environmental damage despite regulatory requirements to minimize impacts. Current mitigation strategies are meant to compensate for lost stream habitat and functions but do not; water-quality degradation caused by mining activities is neither prevented nor corrected during reclamation or mitigation.

Clearly, current attempts to regulate MTM/VF practices are inadequate. Mining permits are being issued despite the preponderance of scientific evidence that impacts are pervasive and irreversible and that mitigation cannot compensate for losses. Considering environmental impacts of MTM/VF, in combination with evidence that the health of people living in surface-mining regions of the central Appalachians is compromised by mining activities, we conclude that MTM/VF permits should not be granted unless new methods can be subjected to rigorous peer review and shown to remedy these problems. Regulators should no longer ignore rigorous science. The United States should take leadership on these issues, particularly since surface mining in many developing countries is expected to grow extensively (32).

References and Notes
1. World Coal Institute, www.worldcoal.org.
2. K. L. Saylor, *Land Cover Trends: Central Appalachians* [U.S. Department of the Interior, U.S. Geological Survey (USGS), Washington, DC, 2008]; http://landcovertrends.usgs.gov/east/eco69Report.html.
3. MTM/VF refers to surface mining operations that remove coal seams running through a mountain, ridge, or hill; it may also refer more broadly to large scale surface mining, including area or contour mining in steep terrain

that disposes of excess rock in heads of hollows or valleys with streams.
4. Debates are conspicuous because of recent high profile federal court cases [e.g., (33)], widely publicized exchanges between the U.S. Environmental Protection Agency (EPA) and the ACOE over permitting decisions, advocacy by non governmental organizations, and protests by miners.
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6. J. D. Allan, *Annu. Rev. Ecol. Evol. Syst.* **35**, 257 (2004).
7. This 5 to 10% issue is based on studies done on many nonmining types of land use change. Thus far, EPA has not done mining specific studies on this "threshold" issue (percentage of watershed mined versus impacts on streams) despite many calls for such data.
8. T. L. Negley, K. N. Eshleman, *Hydrol. Process.* **20**, 3467 (2006).
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18. EPA, *Stream Chemistry Report*, part 2 (EPA Region 3, Philadelphia, PA, 2002); http://www.epa.gov/region3/mtntop/pdf/appendices/d/stream chemistry/MTMVFChemistryPart2.pdf.
19. A. D. Lemly, *Selenium Assessment in Aquatic Ecosystems: A Guide for Hazard Evaluation and Water Quality Criteria* (Springer, New York, 2002).
20. EPA, *Mountaintop Mining/VF Final Programmatic Environmental Impact Statement* (EPA Region 3, Philadelphia, PA, 2005); http://www.epa.gov/region3/mtntop/index.htm.
21. J. M. Conley, D. H. Funk, D. B. Buchwalter, *Environ. Sci. Technol.* **43**, 7952 (2009).
22. S. McAuley, M. D. Kozar, *USGS Report* 5059 (2006); http://pubs.usgs.gov/sir/2006/5059/pdf/sir2006 5059.pdf.
23. M. K. Ghose, S. R. Majee, *Environ. Monit. Assess.* **130**, 17 (2007).
24. M. Hendryx, M. M. Ahern, *Public Health Rep.* **124**, 541 (2009).
25. Mining industry and government organizations recently signed a statement of intent to promote reforestation approaches that improve reclamation [see, e.g., (34)]; however, adoption of recommendations is voluntary. Reforestation of a mined site to premined conditions has not been demonstrated.
26. J. A. Simmons *et al.*, *Ecol. Appl.* **18**, 104 (2008).
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29. P. A. Townsend *et al.*, *Remote Sens. Environ.* **113**, 62 (2009).
30. EPA and ACOE, *Fed. Regist.* **73**, 10 (2008).
31. U.S. District Court, Civil Action No. 3:05 0784, transcript, vol. 3, pp. 34 45; http://palmerlab.umd.edu/MTM/US District Court Civil Action Official transcript Volume III.pdf.
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33. U.S. Court of Appeals for the 4th District, *Ohio Valley Environmental Coalition* et al. vs. *U.S. ACOE* et al., case 07 1255.
34. Appalachian Regional Reforestation Initiative, www.arri.osmre.gov/FRApproach.shtm.
35. This is contribution no. 4368 of the University of Maryland Center for Environmental Science.

David Rider/R3/USEPA/US

01/07/2011 11:16 AM

To	Greg Pond
cc	
bcc	
Subject	Fw: Spruce - EPT composition does not indicate any impact on higher trophic level biota

Greg,

fyi - a wide range of interest in EPT ecosystem services.

Dave

----- Forwarded by David Rider/R3/USEPA/US on 01/07/11 11:13 AM -----

Re: Spruce - EPT composition does not indicate any impact on higher trophic level biota

Terry Master to: Jim_Zelenak, David Rider   01/06/11 11:26 AM

Cc: Laura_Hill, Brady Mattsson, Bob Cooper, "Latta, Steve", Marshall Matt, Robert Mulvihill

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Hi Everyone:

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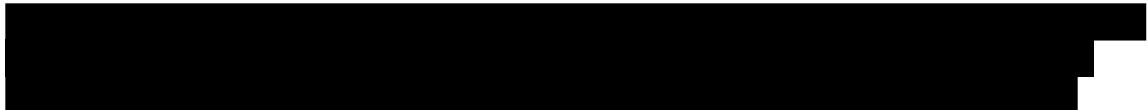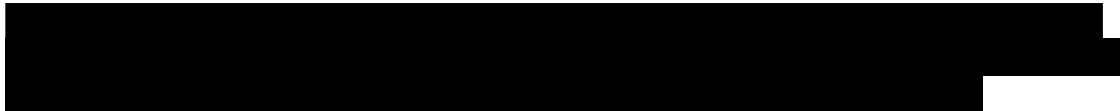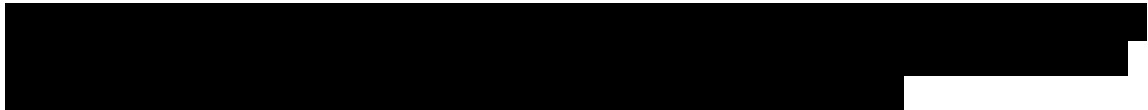
Terry

On 1/6/11 9:34 AM, "Jim_Zelenak@fws.gov" <Jim_Zelenak@fws.gov> wrote:

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[REDACTED]

Cheers!

Jim Zelenak
U.S. Fish and Wildlife Service
West Virginia Field Office
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jim_zelenak@fws.gov

Rider.David@epamail.epa.gov

Rider.David@epamail.epa.gov 01/06/2011 08:26 AM

To

jim_Zelenak@fws.gov

cc

Subject

Spruce - EPT composition does not indicate any impact on higher trophic level biota

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David E. Rider
US Environmental Protection Agency
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Philadelphia, PA 19103-2029
215-814-2787

Learn more about the Office of Monitoring & Assessment at
http://epa.gov/reg3esd1/3ea50.htm <http://epa.gov/reg3esd1/3ea50.htm>

DipperDiets.pdf

The diet of breeding dippers Cinclus cinclus cinclus and their nestlings in southwestern Norway

S. J. Ormerod, Svein Efteland and Leif E. Gabrielsen

The diet of dippers in south west Norway was investigated by faecal analysis during the 1985 breeding season. Overall, the diets of adults and nestlings were similar and consisted mostly of nymphs and larvae of Baetidae (mayflies), Leuctridae/Nemouridae (stoneflies), Hydropsychidae, Limnephilidae and Rhyacophilidae (caddisflies). However, strong trends were apparent with nestling age: large items such as caddisflies declined in adult diet but increased in nestling diet as the chicks grew. The pattern probably reflected the growing energy demands of the brood in a central-place. Because some of the items of dietary importance are scarce in acidic streams, we stress the need for research on the influences of acidification on the ecology of Scandinavian dippers.

S. J. Ormerod, Dept of Applied Biology, Univ. of Wales, Institute of Science and Technology, P.O. Box 13, Cardiff CF1 3XF, U.K. S. Efteland, N-4060 Kleppe, Norway. L. E. Gabrielsen, N-4063 Voll, Norway.

1. Introduction

Dippers Cinclus cinclus are passerine birds unique in their close association with rivers from which they feed almost exclusively (Jost 1975, Ormerod 1985a, Spitznagel 1985, Ormerod and Tyler 1986). Dietary studies in Europe have recently revealed much about their foraging ecology, although none of these studies has involved the nominate race and there has been no systematic account of the diet of dippers in Norway (Ormerod 1985a,b, Ormerod and Perry 1985, Spitznagel 1985).

The autecology of dippers has also received much attention in view of possible influences on their distribution and breeding performance by surface-water acidification (Ormerod et al. 1985a, 1986a, Kaiser 1985). In Wales, Ormerod et al. (1986a) concluded that influences which increased the acidity and aluminium concentrations in soft-water streams would have a detrimental effect on dipper populations, probably by altering the quantity or quality of their food. However, there has been no published assessment of possible influences by acidity on dippers in Scandinavia despite strong evi-

dence of acidification and subsequent effects on aquatic fauna, including water birds (Overrein et al. 1980, Eriksson 1984). Dietary studies on Scandinavian dippers, therefore, seem desirable.

In this paper, we describe the diet of breeding dippers and their nestlings in Rogaland, south west Norway, during 1985.

2. Study area

Dietary studies were undertaken at 10 sites on 3 main river systems (Imsvassdraget, Figgjovassdraget, Havassdraget) within an area of about 1000 km² (approximately 58°46′N 5°53′E) to the south east of Stavanger. The location has been generally described elsewhere (Efteland and Kyllingstad 1984).

Few water quality data are available on the study rivers, although lakes in their catchments have low to moderate acidities (pH 5.4–6.8, rarely 8; e.g. Henrikson et al. 1981, Faafeng 1983). Land uses are dominated by agriculture (mostly grazing), with some woodland (mostly birch, Betula). Overall, the water courses are unproduc-

Tab. 1. Regressions ($\log_{10} y = a + bx$) of dry weight (mg) on mandible size ($\mu m \times 10^{-1}$) for invertebrates preyed upon by dippers.

Taxon	b	a	x measurement	r^2
Baetidae	0.068	−2.41	width	0.88
Leuctridae/Nemouridae	0.065	−1.73	width	0.94
Perlidae/Perlodidae	0.014	−0.72	length	0.85
Hydropsychidae	0.022	−0.96	length	0.63
Rhyacophilidae	0.030	−1.15	length	0.76
Polycentropopodidae	0.012	−0.88	length	0.85
[1]Limnephilidae	0.028	−0.76	length	0.83
Simuliidae	0.038	−1.74	length	0.89

[1] *Potamophylax* and *Halesus*.

tive and dippers bred at abundances of only 1.5–2.2 pairs per 10 km (Efteland and Kyllingstad 1984).

3. Methods

Diet was assessed wholly by faecal analysis using methods described more fully elsewhere (Ormerod 1985a, Ormerod and Tyler 1986). Where possible, faecal pellets were collected from incubating adults, and subsequently from both adults and nestlings of ages up to 17

days. Nests were visited on several occasions between 21 April and 18 May in order to assess synchronous changes in the diets of both adults and nestlings as the latter grew.

In the field, pellets were preserved in 70% methanol. In the laboratory, they were deflocculated for approximately 4 hours in N/2 NaOH before detailed examination at magnifications of X40–X100. Prey were identified to family and quantified by counting mouthparts which maintain their integrity through the dipper gut (Ormerod, unpubl.).

Where possible, the dry weights of individual prey were reconstructed from mouthpart size using the regression relationships in Tab. 1. Although these were derived from invertebrates collected in Britain, many of the same genera occur in Norway and the relationships are unlikely to be inaccurate. Estimates of dietary contributions by weight were then derived by multiplying the number of faecal occurrences for any prey type by its mean dry weight.

4. Results

In total, 85 and 93 faecal pellets were collected respectively from adults and nestlings and they contained the remains of 652 and 827 prey items. Most prey were from

Tab. 2. The diets of breeding dippers and their nestlings in south west Norway in 1985. The values are percentage contributions by number and by dry weight. The mean weights of each prey type are given, with separate values for adults and nestlings where they were significantly different.

Prey type	Mean dry weight (mg)	Adults		Nestlings	
		number	weight	number	weight
Ephemeroptera					
Leptophlebiidae	[1]0.95	0.5	<0.1	0.1	<0.1
Baetidae	1.14	40.0	7.8	43.9	8.3
Ecdyonuridae	[1]2.00	0.2	<0.1	–	–
Plecoptera					
Leuctridae/Nemouridae	2.18	18.8	6.8	13.5	4.9
Perlidae/Perlodidae	1.22; 2.46	1.7	0.3	3.4	1.4
Trichoptera					
Hydropsychidae	6.21	4.2	5.1	10.9	11.2
Polycentropopodidae	1.18	1.1	0.2	0.8	0.2
Rhyacophilidae	4.62	10.4	8.3	13.5	10.4
Glossosomatidae	4.63	1.5	1.2	0.2	0.2
Limnephilidae	47.37; 38.51	8.3	67.4	9.5	61.1
Sericostomatidae	[1]8.12	0.3	0.4	0.5	0.6
Goeridae	[1]4.82	1.8	1.5	1.8	1.4
Diptera					
Simuliidae	0.46	9.2	0.6	1.4	<0.1
Chironomidae	[1]0.27	0.3	<0.1	–	–
Tipulidae	[1]2.48	–	–	0.1	<0.1
Coleoptera					
Elminthidae	[1]0.25	0.2	<0.1	–	–
Hymenoptera					
Formicoidea	N/A	1.1	N/A	–	–
Total items		652		827	

[1] Mean weights from other studies (Ormerod 1985a). All others were reconstructed from mouthparts in faeces (see Tab. 1).
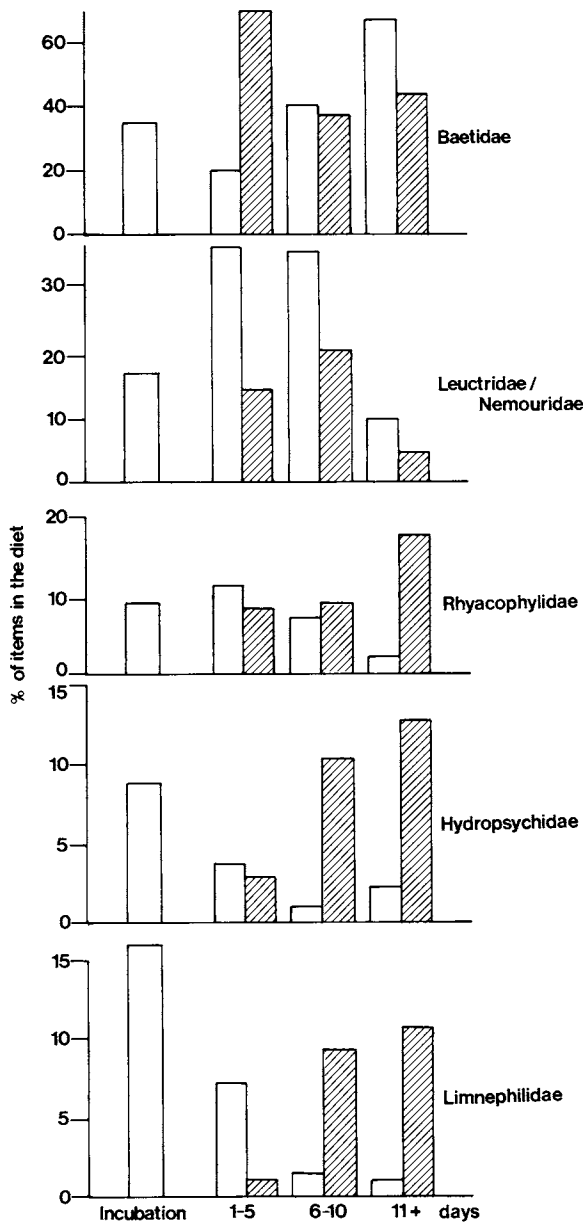
Fig. 1. Changes with nestling age (days) in the percentage contribution by invertebrates to the diets of adult (clear) and nestling (shaded) dippers.

the caddis larvae Limnephilidae, Rhyacophilidae and Hydropsychidae, with baetid mayflies providing 7–8% of the dietary intake (Tab. 2).

Strong differences between the diets of adults and nestlings became apparent when nestling age was taken into account. In particular, the caddis larvae Rhyacophilidae, Hydropsychidae and Limnephilidae increased in nestling diet, but declined in adult diet, as the nestlings grew; the reverse trend was apparent in Baetidae which appeared to be particularly important to young nestlings (Fig. 1). There was some evidence that this pattern reflected prey size: the ratio P_iN/P_iA (a modified forage ratio, in which P_i is the percentage of prey type i in the diets of nestlings (N) or adults (A)) correlated positively with prey weight in older nestlings, but negatively in younger nestlings (Fig. 2). Dippers therefore appeared to select large invertebrates in order to feed nestlings over 5 days old, but they used these in self-feeding during incubation and when nestlings were small.

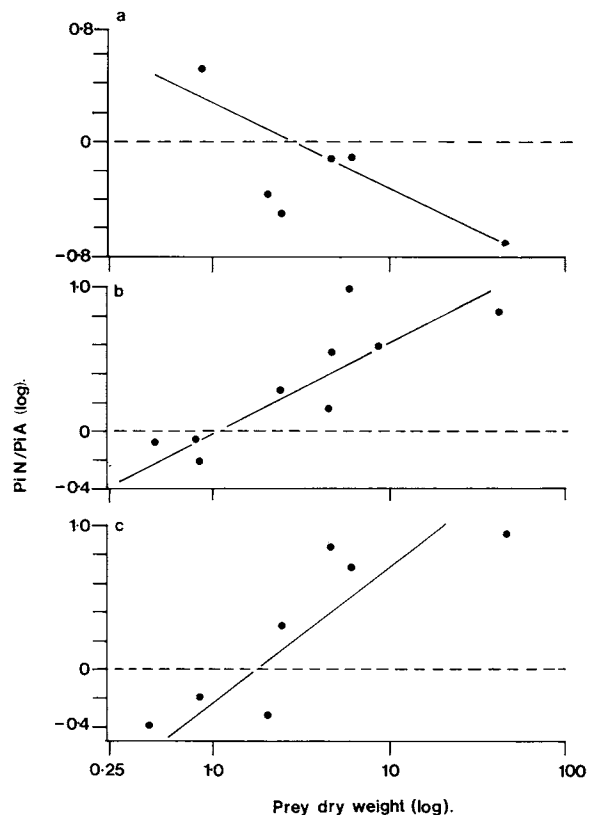Because some of the dietary changes with nestling age

the aquatic stages of invertebrates, and no remains of aerial insects, fish or oligochaetes were found (Tab. 2).

For all the samples combined, there was a strong similarity between the diets of adults and nestlings, both in terms of numerical contributions ($r_s = 0.871$, n = 17, $P < 0.001$) and dry weight ($r_s = 0.898$, n = 16, $P < 0.001$). The most common items were baetid mayflies, leuctrid/nemourid stoneflies, and the caddis larvae Rhyacophilidae, Hydropsychidae and Limnephilidae. Simuliid larvae were common only in adult diet (Tab. 2). The major contributions by weight were from

Fig. 2. Relationships between the ratio P_iN/P_iA and prey weight for three nestling age intervals: a) 1–5 days old ($r_s = -0.521$, N.S.); b) 6–10 days old ($r_s = 0.881$, $P < 0.01$); c) 11+ days old ($r_s = 0.928$, $P < 0.001$). P_iN and P_iA are the percentages of prey type i in the diets of nestlings and adults, respectively.

Tab. 3. The weights of prey (within groups) eaten by adult and nestlings over 5 days old. The weights (mg) were reconstructed from remains in faecal pellets using Tab. 1. The values in parentheses are 95% C.I. and sample size (note geometric mean).

Prey type	Adults	Nestlings	t
Baetidae	1.07 ($\times\atop\div$ 1.16; 97)	1.30 ($\times\atop\div$ 1.13; 136)	1.95[NS]
Leuctridae/Nemouridae	2.18 ($\times\atop\div$ 1.10; 95)	2.16 ($\times\atop\div$ 1.24; 26)	0.11[NS]
Perlidae/Perlodidae	1.22 ($\times\atop\div$ 1.29; 11)	2.46 ($\times\atop\div$ 1.86; 14)	4.37***
Rhyacophilidae	4.24 ($\times\atop\div$ 1.65; 12)	4.69 ($\times\atop\div$ 1.48; 36)	0.63[NS]
Hydropsychidae	5.67 ($\times\atop\div$ 1.23; 29)	6.78 ($\times\atop\div$ 1.15; 29)	1.45[NS]
Limnephilidae	47.37 ($\times\atop\div$ 1.10; 65)	38.51 ($\times\atop\div$ 1.120; 34)	2.17*

 * $P < 0.05$
*** $P < 0.001$

appeared to be related to prey size, the weights of items in the diets of adults and older nestlings (>5 days) were compared within invertebrate groups. In 4 out of 6 taxa for which a comparison was possible, adults fed larger individuals to their nestlings than they ate themselves (Tab. 3). However, in only one case was the difference statistically significant. Additionally, there was one instance (Limnephilidae) of adults eating significantly larger items than nestlings (Tab. 3).

5. Discussion

In this study, mayfly nymphs and caddis larvae respectively provided 40.7% and 28.1% of the diet of adults, and 44.0% and 37.2% of the diet of nestlings. These results generally confirm those from elsewhere in Europe on dipper diet: caddis larvae and mayfly nymphs respectively provided 9–68% and 25–77% of the items eaten by breeding adults, with corresponding values for nestlings of 10–79% (caddis) and 10–64% (mayflies) (Jost 1975, Ormerod 1985a, 1985b, Ormerod and Perry 1985, Spitznagel 1985). It is noteworthy that the abundance of breeding dippers along Welsh streams was strongly related to the abundances of these same invertebrate groups (Ormerod et al. 1985a, 1985b, 1986a).

Changes in the diet of growing chicks have been recorded in several other passerines (Gibb and Betts 1963, Royama 1966, Best 1977, Johnson and Best 1982). Similarly, in Wales and central Germany, large items such as caddis larvae became increasingly frequent in the diet of dipper nestlings after day 5, confirming the situation described here (Jost 1975, Ormerod 1985a). Dippers also increase the number of daily feeding visits to the nest as the nestlings grow (Ormerod, unpubl.) and it is likely that these patterns reflect the increasing energy requirements of the brood. Indeed, there would probably be severe time constraints to dippers feeding their chicks with small prey (Fig. 3).

Fewer data are available on compensatory changes in the diets of adults (see Fig. 2), although many authors have described size-related differences between the items eaten by adults and nestlings, which probably reflect central-place foraging (Royama 1970, Davies 1977). At least in dippers, foraging decisions concerning

prey-size seemed to be made between taxa, rather than between sizes within taxa (Tab. 3).

Several of the invertebrates and fish which are important in the diets of dippers are known to be sensitive to elevated acidity or aluminium concentrations (e.g. Baetidae, Hydropsychidae, Cottidae; Sutcliffe and Carrick 1973, Stoner et al. 1984, Engblom and Lingdell 1984, Ormerod et al. 1986a, 1987). Probably as a consequence, some dipper populations in Britain and Germany have declined when streams have become more acidic (Ormerod et al. 1985a, 1986a, Kaiser 1985). Similar investigations of the abundance and breeding biology of dippers along acidified water-courses in Scandinavia would now prove valuable.
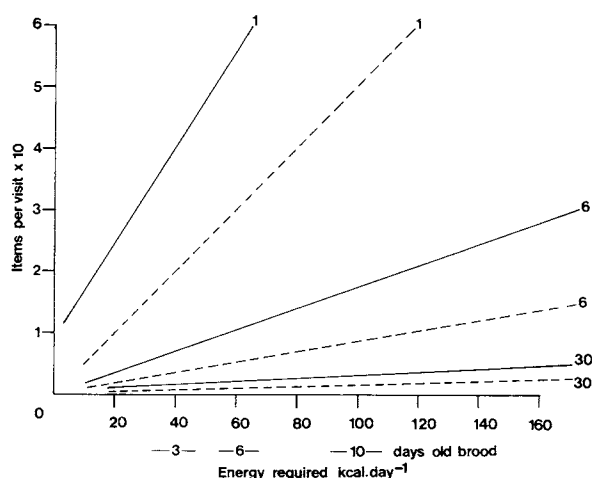

Fig. 3. Theoretical values for the number of items required per visit to satisfy given energy requirements of a brood of 5 dippers. Alternative models have been suggested for two visit regimes (broken line = 400 visit day^{-1}, solid line = 200 visits day^{-1}) and for three prey sizes (1, 6, 30 mg dry weight). Likely energy requirements were calculated from E = 5.661 m$^{0.814}$ (E is given in KJ.d^{-1}, m is brood weight in g) (Kendeigh et al. 1977). Brood weights were from Ormerod et al. (1986b), and invertebrate dry weights were converted to energy using a value of 4.8 Kcal g^{-1} given by Cummins and Wuycheck (1971) for aquatic insects.

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Matthew Klasen/DC/USEPA/US	To	Jeff Lape
01/07/2011 11:23 AM	cc	
	bcc	
	Subject	Fw: Response Supplement #67 Selenium - Support for the 4 ppm whole body threshold

Hi Jeff,

Just wanted to confirm that you guys are working on this, given a hunch that Lynn is out today. I've tried giving her a call to make sure this all makes sense to you (the context can be confusing) but haven't had success so far.

Let me know if you've got any questions about these. (b) (5) ██

Thanks again!

-Matt

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
cell (202) 380-7229
----- Forwarded by Matthew Klasen/DC/USEPA/US on 01/07/2011 11:21 AM -----

From:	Gregory Peck/DC/USEPA/US
To:	Lynn Zipf/DC/USEPA/US@EPA
Cc:	Ephraim King/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Nancy Stoner/DC/USEPA/US@EPA
Date:	01/07/2011 09:26 AM
Subject:	Fw: Response Supplement #67 Selenium - Support for the 4 ppm whole body threshold

Hey Lynn:

I know how busy folks are - but OW is crashing to complete this Spruce Mine veto by Monday so Pete and Lisa can announce on Tuesday. Its going to be a big deal and immediately challenged. We desperately need OST technical assistance regarding the selenium questions identified in Matt's message below consistent with the email I sent folks on Monday. Can we get OST's focus on this today? Please call me if you have any questions.

Best,
Greg
----- Forwarded by Gregory Peck/DC/USEPA/US on 01/07/2011 09:22 AM -----

From:	Matthew Klasen/DC/USEPA/US
To:	Gregory Peck/DC/USEPA/US@EPA
Date:	01/07/2011 09:14 AM
Subject:	Fw: Response Supplement #67 Selenium - Support for the 4 ppm whole body threshold

Greg: Attached are all the questions we need help with from OST. Please also forward along Frank's email below. The critical scientific question for a week has been the Se fish tissue numbers, and we really need that answered from a science perspective.

We have answers for the other two groups of questions (b) (5) ████████████████████████████████████

(b) (5) ███
██████

I'm happy to walk all of this through with someone over there (Lynn?) to make this all make sense. That may be more productive than just sending over.

Thanks,
Matt

2011-01-07 Spruce responses for OST review.docx

Matt Klasen
U.S. Environmental Protection Agency
Office of Water (IO)
202-566-0780
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From:	Frank Borsuk/R3/USEPA/US
To:	Stefania Shamet/R3/USEPA/US@EPA, John Forren/R3/USEPA/US@EPA, Margaret Passmore/R3/USEPA/US@EPA, borsuk.frank@epa.gov
Cc:	Matthew Klasen/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, David Rider/R3/USEPA/US@EPA, David Kargbo/R3/USEPA/US@EPA
Date:	12/29/2010 11:21 AM
Subject:	Response Supplement #67 Selenium - Support for the 4 ppm whole body threshold

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ATTACHMENTS REDACTED - DELIBERATIVE

Peterson et
al 2009
selenium.pdf

Hamilton_2003.pdf

Frank Borsuk, Ph.D.
Aquatic/Fisheries Biologist
Freshwater Biology Team
USEPA-Region 3 (Wheeling Office)
Office of Monitoring & Assessment (3EA50)
Environmental Assessment & Innovation Division
1060 Chapline Street, Suite 303
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Please visit our website at http://epa.gov/reg3esd1/3ea50.htm

Karyn Wendelowski/DC/USEPA/US

01/07/2011 11:25 AM

To   Christopher Hunter

cc

bcc

Subject   edits to App. 1

ATTACHMENT REDACTED - DELIBERATIVE

Spruce Appendix 1 kw edits.doc

Christopher Hunter/DC/USEPA/US	To	David Evans, Jim Pendergast
01/07/2011 12:04 PM	cc	Brian Frazer
	bcc	
	Subject	Fw: Spuce Fact Sheet

FYI

From:	Gregory Peck/DC/USEPA/US
To:	Nancy Stoner/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA, Brian Frazer/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Kevin Minoli, Karyn Wendelowski/DC/USEPA/US@EPA
Date:	01/07/2011 12:03 PM
Subject:	Spuce Fact Sheet

When you have a chance, please review the attached Fact Sheet we'll be using as part of the communications materials to summarize the Spruce Final Determination.

Steph - please don't forget to send me the R3 comments on the draft PR - thanks.

Greg

ATTACHMENT REDACTED – DELIBERATIVE

Mining Spruce Draft Fact Sheet JAN 07 11.doc

		To	Gregory Peck
Karyn Wendelowski/DC/USEPA/US		cc	Kevin Minoli
01/07/2011 12:24 PM		bcc	
		Subject	Re: Spuce Fact Sheet

this looks good - just a few cleanups of extra spaces and then some edits to the very last bullet to tie it to wildlife and mention the downstream effects

ATTACHMENT REDACTED - DELIBERATIVE

Mining Spruce Draft Fact Sheet JAN 07 11kw.docx

Gregory Peck	When you have a chance, please review the atta...	01/07/2011 12:03:44 PM

From:	Gregory Peck/DC/USEPA/US
To:	Nancy Stoner/DC/USEPA/US@EPA, Matthew Klasen/DC/USEPA/US@EPA, Denise Keehner/DC/USEPA/US@EPA, Brian Frazer/DC/USEPA/US@EPA, Christopher Hunter/DC/USEPA/US@EPA, Stefania Shamet/R3/USEPA/US@EPA, Kevin Minoli, Karyn Wendelowski/DC/USEPA/US@EPA
Date:	01/07/2011 12:03 PM
Subject:	Spuce Fact Sheet

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Steph - please don't forget to send me the R3 comments on the draft PR - thanks.

Greg

[attachment "Mining Spruce Draft Fact Sheet JAN 07 11.doc" deleted by Karyn Wendelowski/DC/USEPA/US]

Christopher Hunter/DC/USEPA/US

01/07/2011 12:25 PM

To	Karyn Wendelowski
cc	
bcc	
Subject	Re: new executive summary?

It's in Denise's hands right now, so I think it's still being reviewed, but I'm attaching it here so I can get your comments as well.

ATTACHMENT REDACTED – DELIBERATIVE

Revised Spruce 404c Executive Summary.doc

Chris Hunter
U.S. Environmental Protection Agency
Office of Wetlands, Oceans, & Watershed
(202) 566-1454
hunter.christopher@epa.gov

| Karyn Wendelowski | just didn't want to forget about this - you had m... | 01/07/2011 12:13:49 PM |

From:	Karyn Wendelowski/DC/USEPA/US
To:	Christopher Hunter/DC/USEPA/US@EPA
Date:	01/07/2011 12:13 PM
Subject:	new executive summary?

just didn't want to forget about this - you had mentioned that you were working on a new one in light of Nancy's comments, is it ready for me to review yet?

Here they are. Want to take a quick look or want me to just go ahead and print?

Thanks,
Matt

ATTACHMENT REDACTED - DELIBERATIVE

2011 01 07 Draft Spruce Q&As.doc

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